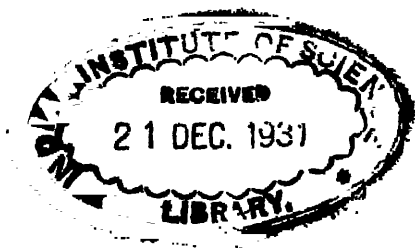


# COLLOID SYMPOSIUM ANNUAL

*(Formerly Colloid Symposium Monograph)*

PAPERS PRESENTED AT THE  
SEVENTH SYMPOSIUM ON COLLOID CHEMISTRY,  
JOHNS HOPKINS UNIVERSITY,  
JUNE, 1929

EDITED BY  
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## FOREWORD

THE SEVENTH COLLOID SYMPOSIUM, sponsored by the Committee on the Chemistry of Colloids of the National Research Council and the Division of Colloid Chemistry of the American Chemical Society, was held at the Johns Hopkins University, Baltimore, Maryland, June 20, 21, and 22, 1929. Professor Frederick G. Donnan of University College, London, was the guest of honor.

At the closing session of the Symposium the following resolution was adopted:

"We, the members of the Seventh Colloid Symposium, desire to put on record our sincere thanks to the Board of Trustees, the President, and the Staff of Johns Hopkins University for their kindness in entertaining the Colloid Symposium, and our appreciation of the foresight shown in all the arrangements made for the conference; also, we desire to express our appreciation of and gratitude for the visit of Professor Frederick G. Donnan, F. R. S., whose presence has contributed so much to the success of the Meeting."

Since the beginning of the Symposium in 1923 the papers presented at the Meetings have appeared annually under the title, "Colloid Symposium Monograph." With the current issue of the annual volume, the title becomes, "Colloid Symposium Annual."

The Eighth Colloid Symposium will be held at Cornell University June 19, 20, 21, 1930.

HARRY B. WEISER.

HOUSTON, TEXAS.





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# COLLOID SYMPOSIUM ANNUAL

## THE SCATTERING OF LIGHT IN SOLS AND GELS

BY F. G. DONNAN AND K. KRISHNAMURTI

### I. INTRODUCTION

DURING recent years a great many investigations, both theoretical and experimental, on the scattering of light in gases and liquids and in colloidal systems have been carried out. It is not the purpose of the present paper to give any survey of the extensive scientific literature relating to this subject, the object being rather to give a short account of some of the results which have been obtained recently at University College, London. Some three years ago an extensive programme of investigation was planned, relating to the measurement of the light scattered by colloid sols and gels and to the determination of the depolarization coefficient of this scattered light. These investigations have been extended already to the sols and gels of agar, gelatin, silicic acid, and sodium oleate. Since an account of all the results so far obtained would take up an undue amount of space and time, it is proposed on the present occasion to confine the discussion to the results obtained with agar sols and gels.

The internal structure of gels and the nature of the sol-gel transformation are subjects of great interest to the student of colloid chemistry and physics. Although these matters have been the object of intensive investigation by ultramicroscopic and other methods during recent years, the systematic measurement of light scattering comes as a welcome aid in the elucidation of these difficult problems. This has been already demonstrated by the work of previous investigators in this particular field, amongst whom may be mentioned Arisz,<sup>1</sup> and Kraemer.<sup>2</sup>

<sup>1</sup> Kolloidchem. Beihefte, 7, 22 (1915).

<sup>2</sup> Kraemer and Dexter: J. Phys. Chem., 31, 764 (1927).

The starting point of all such investigations is the famous equation of Lord Rayleigh,

$$I = \frac{9\nu\pi^2 v^2 A^2}{\lambda^4 x^2} \left( \frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2} \right)^2 \sin^2 \theta$$

where  $I$  = intensity of the scattered light at a distance  $x$  from the scattering particle.

$v$  = the volume of the scattering particle.

$\nu$  = the number of particles contained in unit volume.

$\lambda$  = the wave length of the incident light.

$A$  = the amplitude of the incident light.

$n_1$  = the refractive index of the particles.

$n_2$  = the refractive index of the dispersion medium.

$\theta$  = the angle between the incident and diffracted beams.

If we keep the wave-length and intensity of the incident light constant and measure the light scattered at right angles to the incident beam, the Rayleigh equation may be written in the form

$$I = k\nu v^2 \left( \frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2} \right)^2$$

where  $k$  is a constant. Finally, if, as a first approximation, we neglect any changes in the expression in brackets (due to changes in  $n_1$  and  $n_2$ ), we can write the Rayleigh equation in the simple form

$$I = \text{const.} \times \nu v^2$$

The scattered light will therefore increase as the number and size of the scattering particles increase.

As is well known, the equation of Lord Rayleigh relates to the case where the particles are many times smaller than the wave-length of light and are optically isotropic and distributed at random. Many subsequent investigations, both theoretical and experimental, have been carried out to test and to extend Rayleigh's theory. It will be sufficient here to refer to the theoretical investigations of Mie,<sup>3</sup> Gans,<sup>4</sup> and Schouleykin,<sup>5</sup> and the work of Mecklenburg,<sup>6</sup> Tolman,<sup>7</sup> Steubing,<sup>8</sup>

<sup>2</sup> Ann. Physik., 25, 377 (1908).

<sup>3</sup> Ann. Physik., 37, 881 (1912); 47, 270 (1915); 62, 331 (1920); Z. Physik., 17, 353 (1923); 30, 231 (1924).

<sup>4</sup> Phil. Mag., 48, 307 (1924).

<sup>5</sup> Kolloid-Z., 14, 172 (1914); 15, 149 (1914); 16, 97 (1915).

<sup>6</sup> J. Am. Chem. Soc., 41, 297, 575 (1919).

<sup>7</sup> Ann. Physik., 26, 329 (1908).

Isnardi,<sup>9</sup> Pokrowski,<sup>10</sup> Blumer,<sup>11</sup> and others. Many of these investigations have been concerned with the "depolarization" of the scattered light, that is to say, the ratio of the scattered light which is unpolarized to that which is polarized. According to Rayleigh's theory, the scattered light will be completely polarized in a direction perpendicular to the incident beam. This result does not hold good, however, for relatively coarser particles, and, moreover, the proportion of the scattered light which is polarized has been found to depend on the shape of the particles. As a consequence of these investigations, we shall assume in the present paper that the depolarization of the scattered light will increase with increase in size of the particles, and will diminish as the spherical symmetry of the particles increases. In the results to be given later, the depolarization will be expressed as the ratio of the intensity of the unpolarized to that of the polarized light, multiplied by 100. Although the equation of Lord Rayleigh applies only to very small particles and is subject to various limitations, we shall also assume in the present paper that an increase in the amount of scattered light indicates an increase in the number or size or, in general, the total volume of the scattering particles. We assume therefore that we are dealing with sufficiently small particles, and we neglect any effects which might be due to changes in refractive index of either the particles or the dispersion medium.

## II. EXPERIMENTAL METHODS

### MEASUREMENT OF THE RELATIVE INTENSITY OF THE SCATTERED LIGHT

I. The apparatus used for the measurement of the relative intensity of the light scattered by the colloidal solutions is described below and shown in Fig. 1.

*P* is the tungsten arc of a pointolite lamp (1000 candle power) enclosed in a big wooden box which is painted inside and out with non-reflecting black. The intense white light is rendered nearly parallel by the lens *L*. This is done by focusing the arc on a distant screen or wall. *C* is a cell with plane parallel faces, containing cold distilled water, which is used to remove the heat rays from the beam of light. (It has been shown that cold water is quite as efficient as alum solution in absorbing heat rays, and it has the advantage that it does not become

<sup>9</sup> Ann. Physik., **62**, 573 (1920).

<sup>10</sup> Z. Physik., **32**, 713 (1925); **33**, 810 (1925); **35**, 633 (1926); **41**, 493 (1927).

<sup>11</sup> Z. Physik., **32**, 119 (1925); **38**, 920 (1926); **39**, 195 (1926).

turbid after long continued use.<sup>12</sup>  $S_1$ ,  $S_2$ ,  $S_3$  are three circular slits placed in the path of the incident beam so as to cut off the stray light.

This arrangement gives an intense, steady parallel beam of light, which passes through the bottle  $B_1$  containing the liquid standard for comparison and then through the bottle  $B_2$  containing the colloidal solution for examination. The bottle  $B_2$  is immersed in a tank with a metal frame fitted with four plates of good glass, which have been tested and found to be free from optical defects. Some convenient liquid (usually water) is poured into this tank to serve as a bath, and is maintained at a definite temperature. The bottles  $B_1$  and  $B_2$  are

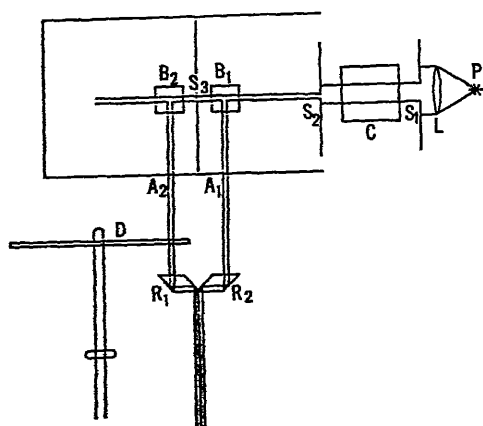


FIG. 1.

rectangular and have parallel sides. They are painted with dull black except in certain positions on the sides for the passage of the incident and scattered beams of light. This is to secure a dark background against which the scattered light may be observed. The beams of light scattered at right angles to the incident beam by the liquid standard and the colloidal

solution are viewed through two small rectangular apertures  $A_1$  and  $A_2$  (about 6 mm.  $\times$  4 mm.) and are matched in intensity by means of the Abney rotating sector photometer  $D$ , in which the angle of the sector could be varied during its rotation.

Some of the important conditions for accurate photometry are:

- (1) The patches of light to be compared should be equal in area.
- (2) They should be contiguous, so that the line of separation\* between the two may disappear when the match is perfect.
- (3) The two patches should be of the same color.

The first of these conditions is satisfied by making the apertures  $A_1$  and  $A_2$  equal in area. The second is fulfilled by the following device:

The scattered beams of light from the liquid and the colloidal solution are initially separated by about 1.5 inches, so that accurate matching is almost impossible. They are brought together so as to be adjacent

<sup>12</sup> Cf. Coblentz: Carnegie Institute Publications, Part VI, 47 (1908).

by interposing in the path of the beams two optical rhombs  $R_1$  and  $R_2$ , which, when placed in a certain position (to be ascertained by trial), cause the two parallel scattered beams to suffer total reflection twice at right angles, so that they finally emerge as two parallel beams adjacent to each other.

The two optical rhombs are of the same material and dimensions, so that the diminution in intensity suffered by the two scattered beams while passing through the rhombs is the same, and hence the ratio of their intensities remains unaltered.

The third condition is satisfied (if the tint of the scattered beam from the sol differs from that of the liquid standard) by introducing a suitable color filter (usually a Wratten photometric blue filter) in the path of the former beam.

The light scattered by some of the sols and many of the gels is much more intense than the faint bluish light scattered by the liquid standard. Hence to facilitate comparison, a neutral tint filter (or photometric blue filter) of the required density is placed in the path of the beam scattered by the colloidal solution or gel.

It is also essential for accurate photometry to prevent any stray light from affecting the eyes of the experimenter. With this object in view, the rotating sector and the support for the optical rhombs are enclosed in a box, painted with non-reflecting black, and open on one side, through which the observations are made, while the opposite side has two apertures through which the two scattered beams enter the "observation box."

The readings were taken when the eye had become accustomed to the darkness of the room. This generally takes a few minutes. The readings obtained were quite reproducible.

#### STANDARDS USED FOR COMPARISON OF THE INTENSITY OF THE LIGHT SCATTERED BY THE COLLOIDAL SOLUTIONS AND GELS

The relative intensity of the light scattered by the colloids is determined by comparing it with the light scattered by a standard. Previous workers on the Tyndall effect in colloids used colloidal suspensions as standards for comparison. Several such standards have been tried by the author, and found to be unsatisfactory, as there was always the uncertainty of obtaining exactly reproducible suspensions. If the suspensions are coarse, they settle down in course of time, or in the case of finely-dispersed colloids a steady change takes place from day to day, due to aging. Further, with the arrangement used for measuring the intensity, it is not possible to use any colloid or coarse suspension, as

this cuts down a good portion of the incident beam of light before this enters the colloid to be examined. Considering all these difficulties, it was thought best to use a liquid as a standard. The advantages of using this are:

(1) The liquid undergoes no change whatsoever even after a considerable length of time.

(2) The light scattered by the liquid, being truly molecular, is the same in all samples of the particular liquid, provided it is pure and dust free.

(3) It can be obtained in a pure condition and rendered dust free by distillation *in vacuo*.

(4) The intensity of the light passing through is very little affected by the liquid.

Carbon disulphide has been found very suitable as a standard, since the light scattered by this liquid is quite considerable compared with other liquids. But when the light scattered by the sol is very feeble, benzene has been used instead. These liquids could be rendered

dust free by distillation *in vacuo* without ebullition.

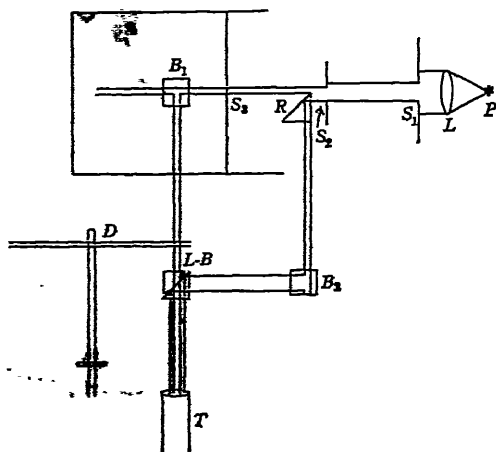


FIG. 2.

II. Another arrangement used for accurately determining the relative intensity of the scattered light is described below and shown in Fig. 2.

*P* is the tungsten arc of a pointolite lamp (1000 candle power), *L* is a lens for obtaining a nearly parallel beam of light, from which the heat rays are

removed by passing it through a cell containing cold distilled water. *S*<sub>1</sub> and *S*<sub>2</sub> are circular slits of suitable diameter. One portion of this beam of light passes through another slit *S*<sub>3</sub> and then through the bottle *B*<sub>1</sub> containing the colloidal solution or gel. The other portion is reflected at right angles by means of a totally-reflecting prism *R*, and passes through the bottle *B*<sub>2</sub> containing the standard. The bottle *B*<sub>1</sub> is immersed in a tank fitted with glass sides and contain-



ing water which is maintained at any desired temperature. The beams of light scattered by the colloid and the standard, which are perpendicular to one another, are brought into juxtaposition by means of a Lummer-Brodham cube, L.B., and are matched in intensity by means of the Abney rotating sector photometer.  $T$  is an observation telescope.

The standard used in the bottle  $B_2$  is usually a liquid, but, when the light scattered by the colloid under examination is very intense, a clear silicic acid gel, which has been kept for a long time to make sure that it suffers no further changes due to aging, is used instead. To facilitate comparison, suitable light filters (neutral tint or photometric blue) of the required density are placed in the path of the beam scattered by the colloid.

As pointed out before, it is essential for accurate photometry to prevent any stray light from affecting the eyes of the experimenter. Hence, the rotating-sector and the support for the Lummer-Brodham cube are enclosed in a box, painted with non-reflecting black. The scattered beams enter the observation box through two suitable apertures.

### MEASUREMENT OF THE DEPOLARIZATION OF THE SCATTERED LIGHT

The degree of depolarization of the scattered light is determined by means of the apparatus shown in Fig. 3, and described below.

The scattered light is observed through a double image Wollaston prism  $W$ , which gives two images whose intensities are in the same ratio as the (polarized) components of the scattered light. These two images are equalized in intensity by rotating the nicol  $N$ , which is mounted in a brass tube  $T$ . Attached to the tube  $T$  is a pointer  $P$ , the free end of which moves round a circular scale graduated in degrees.

As the nicol is rotated, two positions can be found in which the images appear to be of equal intensity. If the angle between the two positions of the nicol be  $2\alpha$ , then the ratio of the intensities of the weak component to the strong compo-

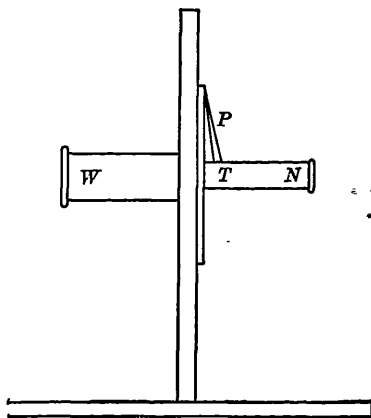


FIG. 3.

ment of the scattered light is given by  $\tan^2 \alpha$ . This gives the depolarization of the scattered light.

Using this apparatus the extent of polarization of the scattered light in a direction perpendicular to the incident beam was determined. A set of readings was obtained and their average taken as the final value.

### III. RESULTS WITH AGAR SOLS AND GELS

The agar sols were prepared in the following manner. A weighed quantity of agar (with an ash content of 2.1 per cent) in the form of fine powder was stirred with the required amount of conductivity water. The mixture was brought to the boiling point with frequent stirring, the water lost by evaporation being made up by the addition of the requisite amount. The sols so obtained were turbid, but were rendered quite clear by filtering through filter paper in a hot funnel. The filtrate is collected in the bottle used for the measurement, which can be immersed in hot water, if necessary, to prevent the sol from setting to a gel. The filtration is extremely tedious in the case of sols of more than 1 per cent concentration.

When an agar sol of as low a concentration as 0.5 per cent is cooled to about 35°, it sets to a gel. On heating, it "liquefies" again, but not until a temperature of about 90° is reached. Below this temperature the gel does not liquefy, however long it may be heated. These sols thus show marked hysteresis. This fact enables us to obtain such systems in either a sol or gel condition at any temperature between 35° and 90°. The following data (Table 1) show the intensity and the depolarization of the light scattered by a 1 per cent agar sol at temperatures ranging from 80° to 25°. The sol sets to a gel at about 33°, though it is possible to obtain a gel by keeping the sol at 35° for a considerable time.

The following facts may be noted. The figures in the second column (i.e., the Tyndall numbers referred to  $CS_2$ ) show that there is no change in the scattered light until about 35°, when it begins to increase rapidly. The depolarization shows no change down to 33°. At about 31° there is a small but perceptible decrease, whilst at lower temperatures there is a steady increase in the proportion of unpolarized light. The increase in the scattered light indicates an increase in the number and/or size of the colloid aggregates or micelles. This increase sets in before the sol-gel transformation occurs, and it continues long after the whole system has set to a firm gel. There is no abrupt change just at the point of gelation. The interpretation of the changes in the depolarization of the scattered light is more difficult, though these

changes are highly significant. We are probably safe in assuming that the steady increase in the depolarization (from about  $30^\circ$  down to  $18^\circ$ ) is due to the increase in size of the colloid particles or micelles. As pointed out in the introduction, there is, however, a factor which causes a *diminution* in the depolarization, namely an increase in the spherical symmetry of the colloid particles. We might perhaps venture the following hypothesis to explain the observed changes in the depolarization. When, with falling temperature, there begins a rapid increase in the intensity of the scattered light, this is due in the first instance to the

TABLE 1—1 PER CENT AGAR

Temperature	Intensity ( $CS_2=1$ ). (Tyndall Number)	Depolariza- tion	Temperature	Intensity ( $CS_2=1$ ). (Tyndall Number)	Depolariza- tion
$75^\circ$	10.5	7.2	$31^\circ$	44.0	6.2
70	10.5	7.2	30	60.7	8.2
60	10.6	7.2	29	70.4	9.4
50	10.6	7.2	27	88.0	10.6
40	10.9	7.2	25	98.2	12.3
35	14.0	7.2	18	110.0	16.3
33	35.2	7.2			

formation of a large number of colloid particles from a polydisperse system in which a considerable, if not a large, proportion of the agar may be molecularly dispersed. These micelles then begin to grow in size with falling temperature, owing to the condensation of the agar upon them. Although this condensation and increase in size will sooner or later lead to an increase in the proportion of the unpolarized light, the initial effect may be such an increase in the spherical symmetry of the numerous first formed colloid micelles that the depolarization at first diminishes.

We may now turn to the study of the gel-sol transformation. By heating an agar gel to a temperature of about  $90^\circ$ , it can be converted into a sol which possesses the same light-scattering capacity as the original sol. Table 2 contains the results for the intensity and depolarization of the light scattered by a 1 per cent agar gel at different temperatures.

It is evident that the light scattering capacity of the agar gel does not undergo any appreciable change till about  $40^\circ$ . Above this temperature both the depolarization and intensity of the scattered light

gradually decrease. Thus, although the gel remains quite firm until a temperature of about  $90^{\circ}$  is reached, the colloidal micelles contained in the gel undergo a progressive diminution in bulk. Apparently, as the temperature is raised, more and more of the material constituting the gel micelles passes into the intermicellar liquid, until finally the structure or framework constituting the gel disappears and we obtain a sol which may be polydisperse and may contain a large proportion of the agar in a molecularly or nearly molecularly disperse form.

Even a superficial examination of agar sols and gels of the same total concentration and at the same temperature reveals that the gels are more opalescent than the sols.

TABLE 2—1 PER CENT AGAR GEL

Temperature	Intensity ( $CS_2=1$ )	Depolarization	Temperature	Intensity ( $CS_2=1$ )	Depolarization
$15^{\circ}$	110.0	16.0	$50^{\circ}$	97.7	14.0
20	110.0	16.0	60	88.0	11.2
30	110.0	16.0	70	73.5	9.7
40	107.4	15.5	75-80	58.5	

In Table 3 are given measurements of the light scattered at various temperatures by agar sols and gels containing 1 per cent of agar. At each temperature, measurements were made after equilibrium had been attained, *i.e.*, when no further change in the Tyndall number occurred after keeping the sol or gel for several hours at the given temperature.

It will be noticed that at all the temperatures observed the gel scatters much more light than the corresponding sol of the same total agar concentration, though this difference tends to diminish as the temperature rises. In the temperature range given in Table 3, the 1 per cent agar sols exhibit the relatively low light-scattering power previously noted. It is quite possible that these sols may contain a considerable proportion of the agar in a molecularly or nearly molecularly disperse form, whilst the gels contain the relatively large colloid particles or micelles which form in the sols at lower temperatures. The high scattering power of the gels might be also due in part to another cause (suggested by Hatschek), namely that gelation is due to the segregation of a phase much richer and an aqueous phase much poorer in agar than the sol. Such an action would produce a considerable difference in the refractive indices of the gel particles and the intermicellar liquid.

So far we have paid no attention to the effect of concentration. Table 4 shows this effect in the case of agar sols.

It will be seen that the intensity of the scattered light in the sol state is fairly proportional to the concentration in the case of the 0.2 per cent and 0.5 per cent sols; with sols of higher concentration the ratio, Tyndall number/concentration, falls off gradually. Another

TABLE 3—1 PER CENT AGAR

Temperature	I (Sol)	I (Gel)	I (Gel)/I (Sol)
70°	10.5	73.5	7.0
50	10.6	88.0	8.3
60	10.6	97.7	9.2
40	10.9	107.4	9.9

TABLE 4—AGAR SOLS

Concentration (Per Cent)	Intensity of Scattered Light ( $CS_2=1$ )			
	60°	50°	40°	35°
0.2	2.6	2.6	2.5	2.6
0.5	6.7	6.5	6.5	6.5
1.0	10.6	10.6	10.9	14.0
2.0	13.5	13.5	14.7	19.0

fact of great interest is the relatively low light-scattering capacity of these sols.

Table 5 shows the effect of concentration on the intensity of the light scattered by agar gels.

From Table 5 it will be seen that in the case of the 0.5 per cent, 1.0 per cent, and 2.0 per cent agar gels, the intensity of the scattered light, especially at the lower temperatures, is fairly proportioned to the concentration, whereas in the 0.2 per cent gel it is comparatively smaller. A comparison of Tables 4 and 5 shows that the ratio of the Tyndall number in the gel to that in the corresponding sol increases markedly with the concentration. The high value of the scattered light in the more concentrated gels is very significant. It is clear that in these cases we have to deal with systems containing large and numerous colloidal particles.

TABLE 5—AGAR GELS

Concentration (Per Cent)	Intensity of Scattered Light ( $CS_2=1$ )				
	60°	50°	40°	30°	20°
0.2	12.8	13.8	14.7	16.3	16.3
0.5	46.8	53.3	53.3	55.0	55.0
1.0	88.0	97.7	107.4	110.0	110.0
2.0	176.0	220.0	220.0	220.0	220.0

The light-scattering power of an agar sol above 40° does not undergo any change even after standing for a long time. But at and below 35° the intensity of the scattered light increases with time, until finally a constant value is reached. The time required for such an equilibrium value to be attained depends upon the temperature—the lower the temperature the more rapid the change. This is clearly illustrated by the results given in Table 6.

TABLE 6—AGAR SOL (1 PER CENT)

Temperature 35°

Time (Minutes)	Tyndall Number	Time (Minutes)	Tyndall Number
0	11.0	60	31.4
5	12.6	70	36.7
15	13.3		
20	15.2	80	40.0
30	20.0	100	47.6
40	24.4	250	65.2
50	27.5	After 21½ hours	92.6

Temperature 30°

0	11.0	21	58.7
5	12.1	25	67.7
10	23.2	40	73.3
13	26.7	45	76.5
15	36.7	10	88.0
18	48.9	120	92.6

Thus whilst the time taken by a 1 per cent agar sol at 35° to reach a Tyndall number of 100 is more than 24 hours, this value is attained in less than half an hour at 25°.

In an earlier part of this paper some account was given of the change in the depolarization of the light scattered by a 1 per cent agar sol produced by fall of temperature. The following tables show how these changes vary with the concentration of the sol.

In the case of the 2 per cent sol we observe a regular increase in the depolarization as the temperature is lowered below 33°, until finally,

TABLE 7—2 PER CENT AGAR SOL

Temperature	Depolarization	Temperature	Depolarization
60°	8.2	33°	8.2
50	8.2	31	10.6
40	8.2	28	13.9
35	8.2	15	21.7
		(After several hours)	

TABLE 8—1 PER CENT AGAR SOL

Temperature	Depolarization	Temperature	Depolarization
60°	7.2	30°	8.2
50	7.2	29	9.4
40	7.2	27	10.6
35	7.2	25	12.3
33	7.2	18	16.3
31	6.2		

after keeping the sol for several hours at 15°, the depolarization rises as high as 21.7 per cent. In the case of the 1 per cent sol there is a small but perceptible decrease at about 32°, but below this temperature the depolarization steadily increases. This initial decrease, followed by an increase, is more marked in the case of the 0.5 per cent sol, whereas with the 0.2 per cent sol the depolarization decreases steadily with fall of temperature. It is thus apparent that the higher the concentration of the sol the greater is the tendency of the depolarization to increase as the temperature falls. It may also be observed that the change in the depolarization commences several degrees below the temperature at which the intensity of the scattered light begins sensibly to increase.

In consonance with the suggestions made in an earlier part of this paper, the following explanation may be advanced to account for these phenomena. We may regard the agar sol at higher temperatures as a polydisperse system containing a considerable and perhaps a large amount of molecularly dispersed agar. At temperatures in the neighborhood of  $35^{\circ}$  there begins a rapid formation of fresh colloidal particles or micelles. The intensity of the scattered light therefore increases. This is followed by a condensation of the molecularly dispersed agar on the particles already present in the sol, thus increasing their size,

TABLE 9—0.5 PER CENT AGAR SOL

Temperature	Depolarization	Temperature	Depolarization
$60^{\circ}$	7.2	$30^{\circ}$	6.2
50	7.2	28	5.3
40	7.2	25	4.9
35	7.2	20	4.9
32	7.2	10	7.2
		(After several hours)	

TABLE 10—0.2 PER CENT AGAR SOL

Temperature	Depolarization	Temperature	Depolarization
$60^{\circ}$	7.2	$32^{\circ}$	7.2
50	7.2	30	6.2
40	7.2	28	5.8
35	7.2	10	3.8
		(After several hours)	

and for this reason further increasing the amount of scattered light. The change in the depolarization is determined, however, by the shape as well as by the size of the effectively scattering particles. The larger the particles contained in the sol the greater is the depolarization of the scattered light, whilst the more they approach spherical symmetry the less will be the value of this quantity. It is probable that during the growth of the colloid particles they tend to become more spherical, owing to the symmetrical condensation of agar on them. Thus the depolarization is influenced simultaneously by two factors, and whichever of these is the more appreciable will naturally have the greater effect. In the case of the dilute 0.2 per cent sol, the increase in the size



of the particles is slow and comparatively small, whilst their tendency to become more spherical is relatively more pronounced. Hence in this case the value of the depolarization decreases with falling temperature. In the more concentrated sols, however, the particles grow to relatively large dimensions, owing to the condensation or precipitation of a large amount of agar on them. This increase in size has now the greater influence and consequently the depolarization increases as the temperature is lowered.

Besides the shape and size of the particles, the concentration of the system might be expected to have some influence on the value of the depolarization. In this connection the following table of comparative data is of interest.

The figures in this table apply to the region of temperature where the sols have not begun to exhibit any increase in the amount of scat-

TABLE 11

Concentration (Per Cent)	Depolarization	
	Sol State	Gel State
2.0	8.2	21.7
1.0	7.2	16.3
0.5	7.2	7.2
0.2	7.2	3.8

tered light. It is evident that in the case of the sols, the increase in concentration produces little effect on the value of the depolarization. These sols must therefore be very similar as regards the shape and size of their colloidal constituents. The marked increase in the depolarization with increase of concentration in the case of the corresponding agar gels makes it very probable that these gels vary very considerably with respect to the size of their colloid particles, the latter being larger in size the greater the total concentration of the gel.

It will be seen from the results recorded in this paper that the measurements of scattered light and of the degree of depolarization of this scattered light are of considerable assistance in the determination of the bulk and shape of the colloid particles contained in agar sols and gels. These results are also of considerable interest in their bearing on the nature of the sol-gel and gel-sol transformations. We have seen that when an agar sol is cooled there is a marked increase in the quantity of colloid particles or micelles before gelation sets in, and that as the

temperature falls there occurs a great increase in the total volume of these colloid particles long after the sol has set to a firm and elastic gel. Conversely, when the gel is raised in temperature there occurs a progressive decrease in the total volume of the colloid particles, this decrease setting in and progressively continuing long before the temperature is reached at which the gel passes into a sol. It is therefore evident that increases and decreases of the "colloidality" of agar sols and gels occur continuously with continuous variation of temperature and are subject to no abrupt or discontinuous changes corresponding to the usually recognized sol-gel and gel-sol transitions.

Though it would be premature to base on these optical measurements of agar sols and gels any definite theory of the intrinsic nature and differences of sols and gels in general, it is possible that an extension of measurements of this type to a wide range of sols and gels of different and varied substances may contribute in no small measure to a clear understanding of the nature of these important and interesting systems.

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# THE STRUCTURE OF GELATIN SOLS AND GELS

## II. THE ANISOTROPY OF GELATIN GELS<sup>1</sup>

BY S. E. SHEPPARD AND J. G. McNALLY

IN the first paper of this series<sup>2</sup> evidence was given that in gelatin solutions in water, in the sol condition, at temperatures above a certain value—in the case studied, at least above 38° C.—the gelatin is dispersed to molecular dimensions, these molecules being, however, “macro-molecules” of perhaps 10,000 to 30,000 M.W. But, furthermore, in all such aqueous solutions the mean molecular weight is steadily falling, because of hydrolysis, although the rate of hydrolysis, which was constant over the pH range 4.7 to 8.1, was very slight at 40° C. It was concluded from this that in such solutions, the rate of change of fluidity was more fundamentally characteristic of the solution than, *e.g.*, the fluidity (or viscosity) itself. In agreement with this conception, such solutions do not show structure viscosity phenomena,<sup>3</sup> at any rate of large magnitude. From comparative data on the initial hydrolysis at 100° C. of a large number of commercial gelatins, it was deduced that gelatins frequently contain a certain amount of incompletely peptized collagen, and it was suggested that the fundamental process of gelatin formation from collagen is not primarily a hydration, nor a hydrolysis, in the chemical sense of these terms, but essentially a disorientation of the macro-molecules of collagen crystallites. The aggregation process of gelation is on this view an incomplete recrystallization, in which the aggregation or *condensation* process is ahead of the *orientation* process. It was pointed out in 1921 by one of the authors<sup>4</sup> that the peculiarities of the aggregate crystals of silver ammonia bromide produced by the action of gaseous ammonia on silver bromide in gelatin<sup>5</sup> could be explained as due to the

<sup>1</sup> Communication No. 399 from the Kodak Research Laboratories.

<sup>2</sup> Sheppard and Houck: J. Phys. Chem. (In press.)

<sup>3</sup> Cf. Bogue: J. Am. Chem. Soc., **44**, 1313 (1922); Sheppard, Elliott and Sweet: Trans. Faraday Soc., **19**, 261 (1923).

<sup>4</sup> Trivelli and Sheppard: “Monographs on the Theory of Photography,” D. Van Nostrand Company, New York, 1 (1921).

<sup>5</sup> Crystal aggregates or aggregate crystals were produced consisting of dispersed

effect of the colloid in displacing the equilibrium between the tendency to increased density in phase of the molecules (condensation) and the tendency to oriented or ordered distribution in phase (crystallization *per se*).

This conception was originally proposed by Riecke,<sup>6</sup> namely, that the growth of a crystal depends, inherently, on the exertion of both attractive (condensing) and orienting (ordering) forces by the original nucleus on the crystallizing substance. His statement antedated the fuller development of the idea by Haber.<sup>7</sup> It appears to us to be of considerable importance for the phenomena of gel formation in solvated colloids.

The point of view indicated, which stresses gel formation as a result of retarded orientation, appears to be in good agreement with the theory of Trillat.<sup>8</sup> From his X-ray structure investigations this worker considers that a gel has the properties of a super-cooled liquid, in which the loss of thermal energy leaves the molecules with axes distributed more or less at random.

In this communication we bring forward evidence that although such a condition tends to obtain in the ordinary "setting" of gelatin gels, after-treatment of the gels by drying and "cold working" brings into operation the delayed orientation forces.

#### PREPARATION OF GELATIN SHEETS

It was shown previously by Sheppard and Elliott<sup>9</sup> that the swelling of gelatin sheets in water takes place principally in a direction normal to the greatest surface not only for sheets or films dried adhering to rigid plates, but also for sheets dried commercially on wire nets. The principal material used in the experiments to be described consisted of gelatin sheets or films coated on glass and stripped after drying. The following routine was followed in preparing the sheets. For most of the work, Eastman Kodak Company de-ashed gelatin, pH 4.7, was used. An 8 per cent (air-dry basis) gelatin solution was prepared by soaking 8 gm. gelatin in 20 cc. water at room temperature for twelve hours. The jelly was dissolved by heating fifteen minutes until a temperature of 60° C. was reached. Water to make up 100 gm. was then added, and the solution held 1 hour at 60° C. It was coated to definite thickness by crystallites which were themselves oriented, the whole aggregate further approaching a cubical rather than a spherical outline.

<sup>6</sup> Ann. Physik, (4) 3, 545 (1900).

<sup>7</sup> Haber: Z. Elektrochemie, 20, 515 (1914). (Discussion of paper by R. Marc.)

<sup>8</sup> Rev. gén. colloïdes, 6, 89 (1928).

<sup>9</sup> J. Am. Chem. Soc., 44, 373 (1922).

covering with a given amount of the solution a glass plate of definite area pre-coated with cellulose nitrate. The jelly was set in an ice-box, remaining 5 minutes, and then, for standard conditions, dried at 55 per cent R.H. at 25°C. The jellies, prepared with ordinary distilled water, showed a pH of 5.2.<sup>10</sup> After drying, the gelatin sheets were readily stripped from the cellulose nitrate surface.

### SWELLING EXPERIMENTS

Preliminary experiments showed that a square piece of gelatin film on swelling increased in length at the same rate along the four edges of the square. The rate of swelling along one edge could therefore be taken as directly proportional to the whole area increase. This increase in linear dimension was termed the *lateral swelling expansion*, and was measured as follows: The gelatin sheets were cut into strips 0.5 cm. wide and 6.0 cm. long. One end of the strip was fitted with a brass binding strip, and the other end inserted in a clamp. The distance between the clamp and the brass binding was 5.00 cm. The apparatus is shown in Fig. 1. It consisted essentially of a celluloid scale to which was attached the clamp holding one end of the gelatin strip. This strip was kept parallel to the scale by a weight of 0.04 gm. (in air) attached to the brass binding. The strip and scale were entirely immersed in the water or solution, the tube being kept in a thermostat constant to  $\pm 0.02^\circ$  C. All experiments were performed in duplicate, and the results checked to within 1 per cent.

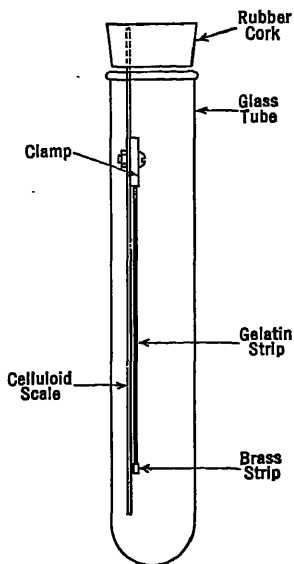


FIG. 1.

*The Lateral Swelling Expansion of Thin Sheets.*—Numerous experiments have demonstrated that the total swelling (increase of weight and volume) of dry gelatin placed in water is always positive. It was, therefore, somewhat surprising to find that the lateral expansion of gelatin sheets might become *negative* to a considerable degree, under certain conditions, although again becoming and continuing *positive* thereafter. The conditions under which this could occur were, therefore, examined more closely, and the negative expansion, or *initial lateral contraction*,

<sup>10</sup> Probably caused by carbonic acid.

was found to depend upon both the temperature of the swelling water and the initial *thickness* of the dried sheet of gelatin.

The lateral swelling expansion was measured for a series of temperatures and initial thicknesses. The curves in Figs. 2 to 10 show the results obtained for sheets varying in thickness from 0.0047 cm. to 0.0090 cm. and for temperatures from 15° C. to 35° C.

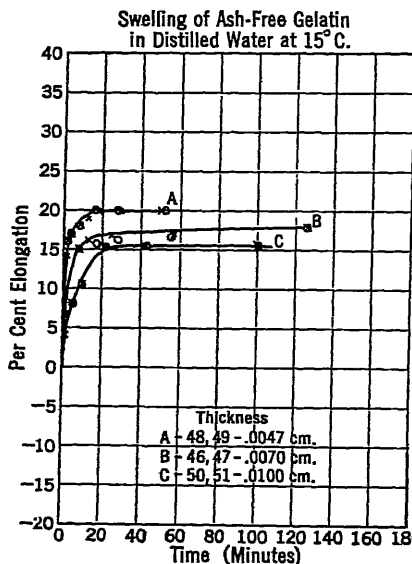


FIG. 2.

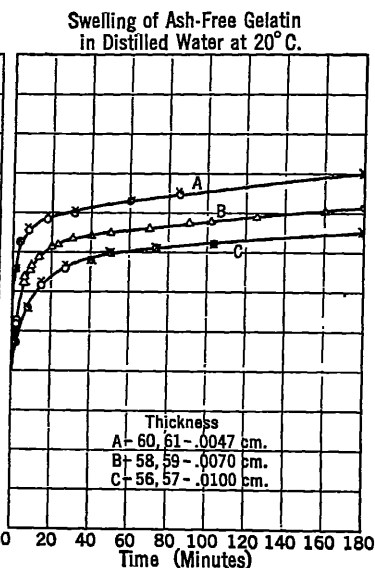


FIG. 3.

From these, and many other confirmatory results not reproduced, the following empirical conclusions are obtained:

(a) At relatively low temperatures, 15° C. and below, ash-free gelatin in distilled water rather rapidly reaches an equilibrium with water, *i.e.*, shows strictly limited swelling.

(b) At higher temperatures the swelling becomes unlimited, in the sense that in the presence of excess of water the jelly breaks up spontaneously into smaller and smaller masses. The question as to the limits of this process, namely, whether it continues to a certain size distribution dependent on the temperature, is under investigation in connection with the plasticity phenomena. It is to be noted that these temperatures of "unlimited swelling" are below the so-called sol-gel transition temperature, *i.e.*, the temperature above which the viscosity continually and continuously decreases.<sup>11</sup> Since

<sup>11</sup> Sheppard and Houck: *Op. cit.*

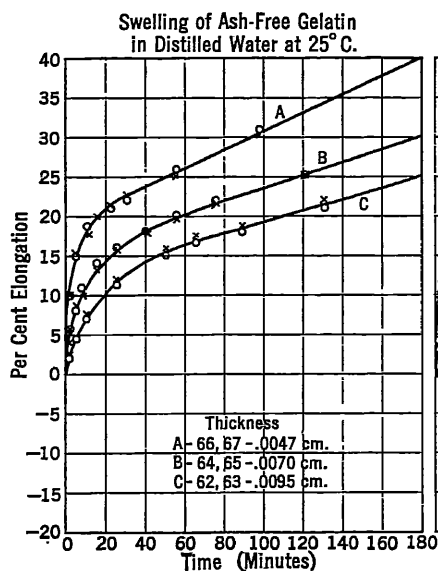


FIG. 4.

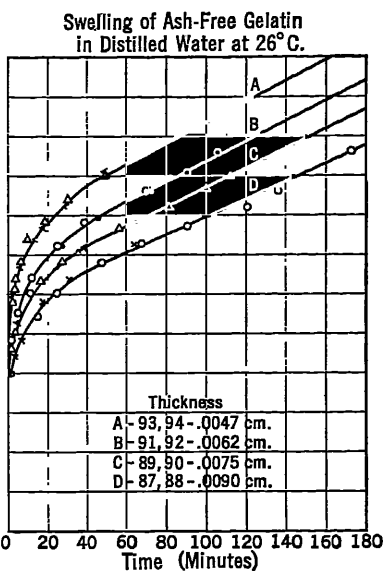


FIG. 5.

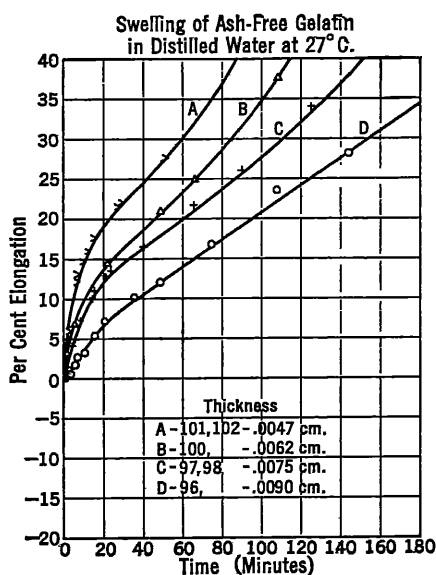


FIG. 6.

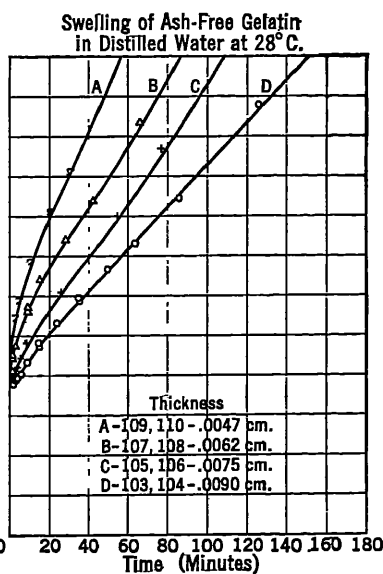


FIG. 7.

# THE STRUCTURE OF GELATIN SOLS AND GELS

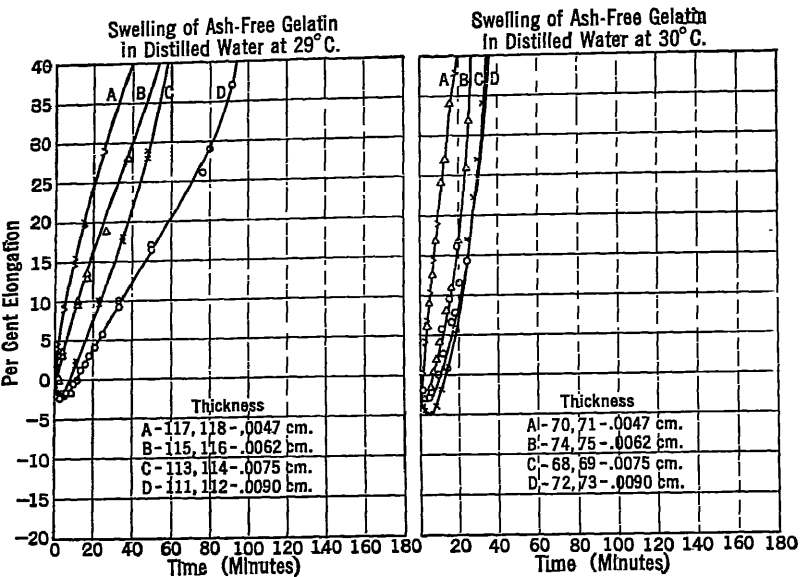


FIG. 8.

FIG. 9.

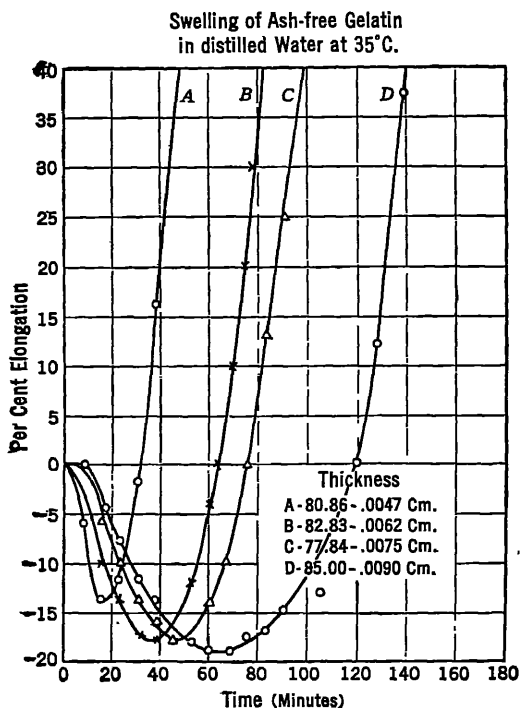


FIG. 10.



it is concluded that below this temperature *gelatinization* is proceeding, it appears likely that the swelling jelly is tending to a specific dispersion limit, but probably depending upon the concentration.

(c) At a certain temperature, for a given thickness of gelatin sheet, the lateral expansion, proceeding to unlimited swelling, is preceded by a period of *initial contraction*. The amount of this initial contraction depends upon both the thickness and the temperatures. Within the range studied, the thicker the sheet, the lower the temperature at which it appeared, and the greater the extent of the contraction before reversal. It is probable that a limit thickness is soon reached, when this relation ceases to hold.

(d) This contraction is occurring while the material is actually absorbing water, *i.e.*, swelling in volume. This was checked repeatedly, and is illustrated in Fig. 11. The most immediate explanation

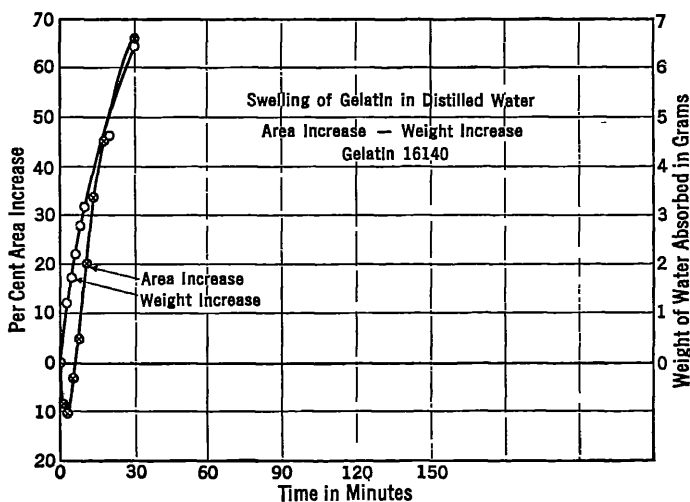


FIG. 11.

of this contraction phenomenon is that it depends upon some kind of residual strain left in the gelatin sheet on drying. Attention has already been drawn by Sheppard and Elliott<sup>12</sup> to the anisotropy of swelling of gelatin as a consequence of residual strains on drying the jelly. Before proceeding to a direct examination of this by optical means, some further evidence may be given from swelling experiments leading to the same conclusion.

<sup>12</sup> J. Am. Chem. Soc., **44**, 373 (1922); Trans. Faraday Soc., **19**, 261 (1923).

*Lateral Expansion of Gelatin Sheets Dried in a Stretched Condition.*—If strains left in gelatin sheets on drying affect the subsequent swelling of the sheet, it should follow that a sheet which had been stretched while still in the swollen jelly, and then dried in this deformed state, should show abnormal dimensional changes when placed in water. To test our theory on this point, the following experiments were carried out.

A sheet of gelatin 0.0125 cm. thick was coated from a 5 per cent ash-free gelatin and dried at 55 per cent R.H. at 25° C. The sheet was then cut into rectangles 11 cm. by 5.5 cm. These strips were then securely clamped along the longer sides in metal grips, and placed in distilled water (pH 6.1) at 23° C. for thirty minutes. At the end of this swelling period, the gelatin was quite elastic, and the sheet was then stretched by moving the brass grips apart and clamping them on a suitable frame. The apparatus was then removed from the water and the gelatin dried again at 55 per cent R.H. and 25° C. A strip 6 cm. wide was cut from the center of the 11-cm. sheet (at right angles to the direction of stretch), and also smaller strips 0.5 by 5.5 cm., the length of the test strips being along the direction of stretch. The dimensions of 2 sheets before and after stretching are given in the following table:

Sheet Number	Length before Stretching	Length after Stretching	Per Cent Elongation
18	5 cm.	6.55 cm.	31
19	5 cm.	8.00 cm.	20

Sheet 18 was 0.0087 cm. thick after stretching, and sheet 19 was 0.010 cm. thick. In Fig. 12 are shown the changes of length (lateral expansions) of sheet 18 when swollen in distilled water (pH 6.0) at various temperatures, and in Fig. 13 the data for sheet 19.

The following important conclusions appear from these curves:

(a) The greater the stretch prior to drying, hence, the greater the residual strain, the lower the temperature at which initial contraction appears.

(b) With increased stretch (and residual strain) the lower the ultimate elongation. In these experiments, the maximum per cent elongation reached did not exceed 7 per cent. By comparison with Fig. 12 it can be seen how greatly the stretching had reduced the lateral expansion.

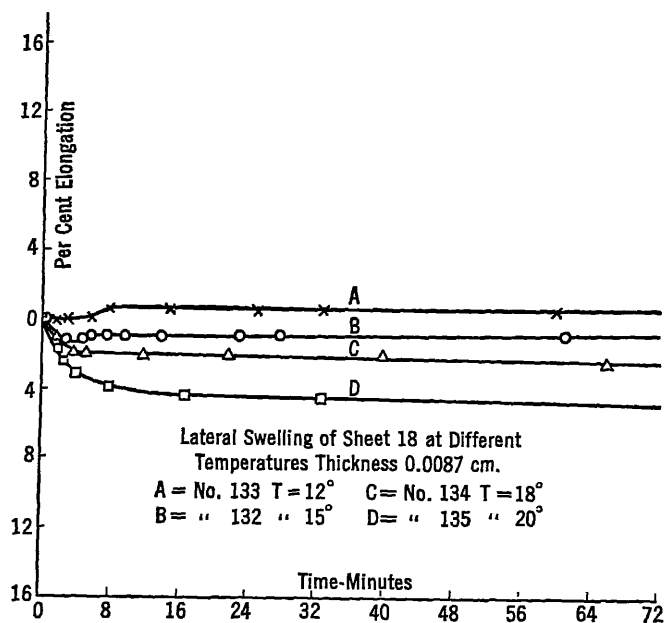


FIG. 12.

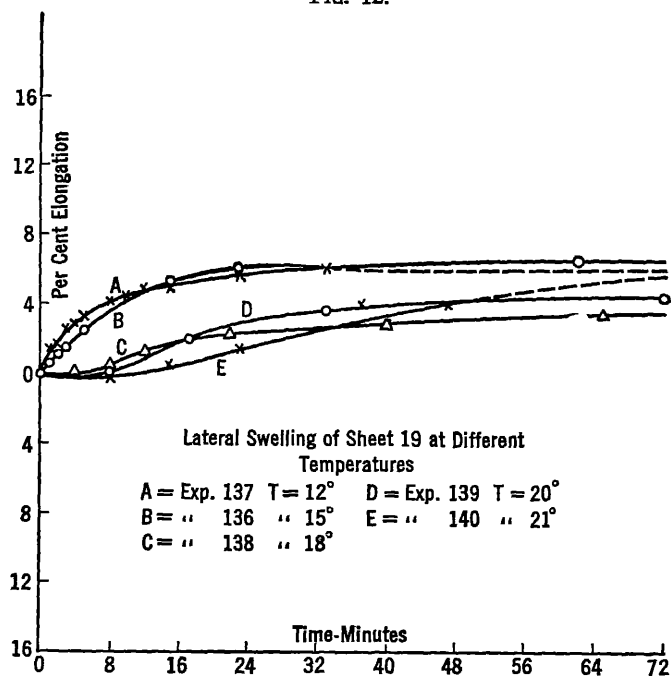
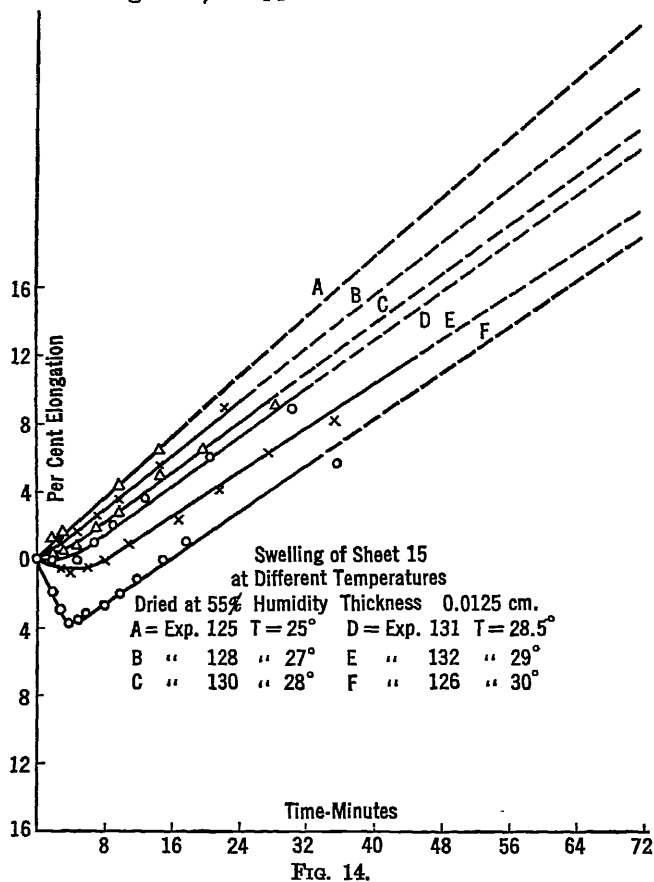


FIG. 13.

## THE STRUCTURE OF GELATIN SOLS AND GELS

(c) In extension of (b) it is apparent that the elongation may even be negative, *i.e.*, the initial contraction may become permanent if the gelatin be greatly strained, and if the temperature of swelling be high enough.

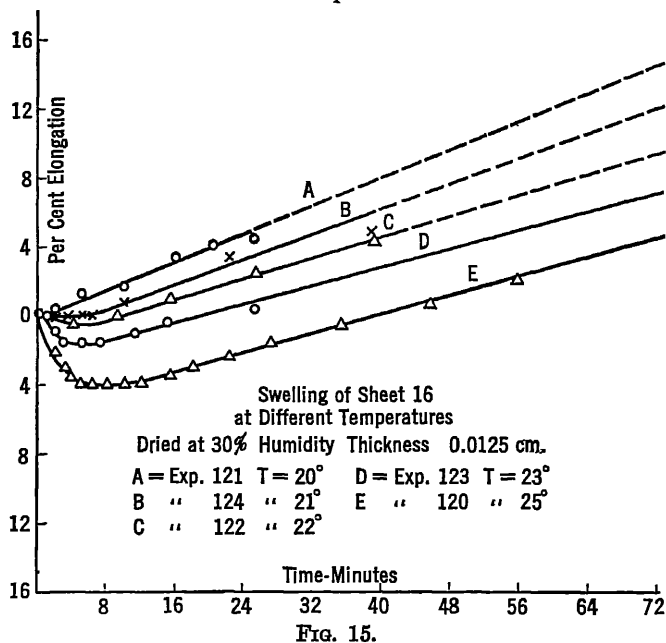
From control experiments on the increase of weight (total swelling) of the stretched gelatin, it appeared that this was somewhat reduced



compared with that of unstretched gelatin. Thus in three hours at 25°C., 1 gm. stretched gelatin had gained 5.4 gm., but unstretched gelatin absorbed 6 to 7 gm. water in thirty minutes. The effect on total swelling, however, being investigated separately. The large residual volume increase of material which, by previous stretching, shows practically no swelling, indicates that the *strained gelatin sheet swells practically equally in a direction at right angles to the direction of deformation.*

*Swelling Anisotropy and Rate of Drying.*—The preceding section has shown that stretching before drying, hence strain in the dried gelatin, produces very marked anisotropy of swelling. We now investigated the rate of drying. Two exactly similar sheets were coated from a 5 per cent solution of ash-free gelatin. Sheet 15 was dried at 55 per cent R.H., and sheet 16 at 30 per cent R.H., both at 25° C. The final thickness in each case was 0.0125 cm. The lateral expansions are shown in Fig. 14 and Fig. 15.

It is evident that the sheet which was dried farther and faster shows initial contraction at the lower temperature.



In a further experiment, sheet 42 was coated from a gelatin solution only slightly above its solidification temperature. It was found to dry more slowly than sheet 43, coated from the same gelatin solution, but at 65° C. Both sheets were 0.00425 cm. thick, and even with such a thin coating, the more rapidly drying film (sheet 43) showed initial contraction at 20° C. in water (Fig. 16).

The behavior of very thin gelatin films after drying in different degrees is shown in Fig. 17.

While neither sheet showed initial contraction, again the sheet dried more severely and rapidly shows a much lower value at equilibrium swelling of the lateral expansion. It is more anisotropic.

## THE STRUCTURE OF GELATIN SOLS AND GELS

*Strain and Orientation.*—These results are in good agreement with the conclusion that gelatin swells most rapidly in directions at right angles to any strains left on drying. It is obvious in the case of the sheets elongated by tension that the forces acting are a tension in the direction of elongation and a pressure at right angles thereto. The following

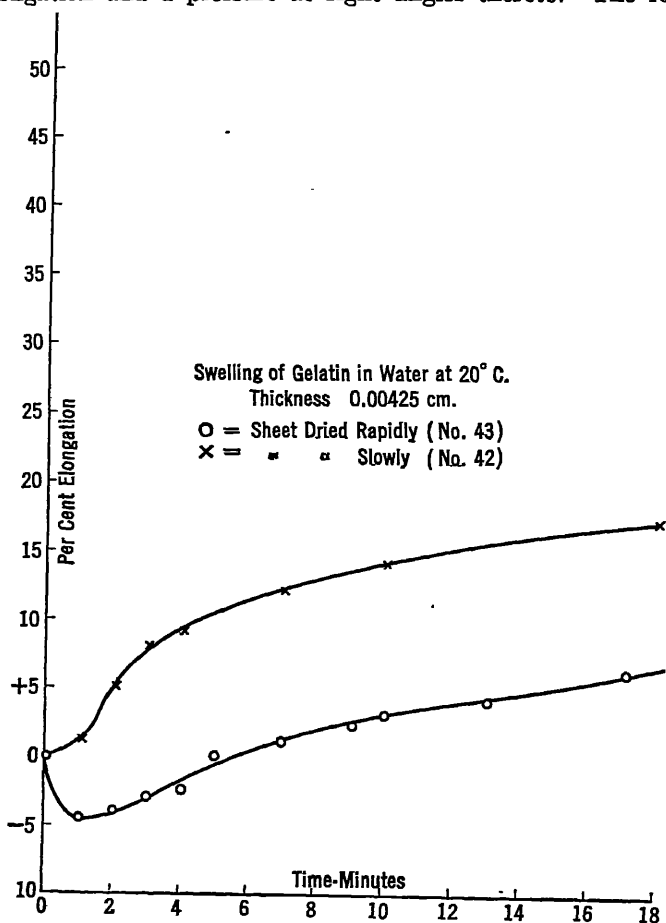


FIG. 16.

considerations of the mechanism of drying of a gelatin jelly, coated and dried on a rigid support, indicate how similar stresses are applied, and a similar residual strain is developed.

The rate of drying of a gelatin sheet depends on:

- The rate of evaporation of water at the gelatin-air interface.
- The rate of diffusion of water from the interior of the gelatin to the surface.

If the drying conditions, *e.g.*, rapid drying and thicker films, allow process (a) to remove water faster than it can be supplied by (b) the contraction of the outer layer of the jelly caused by drying puts a stress on the jelly of the interior. In the case of a sheet this stress is mainly a pressure at right angles to, and a tension parallel to,

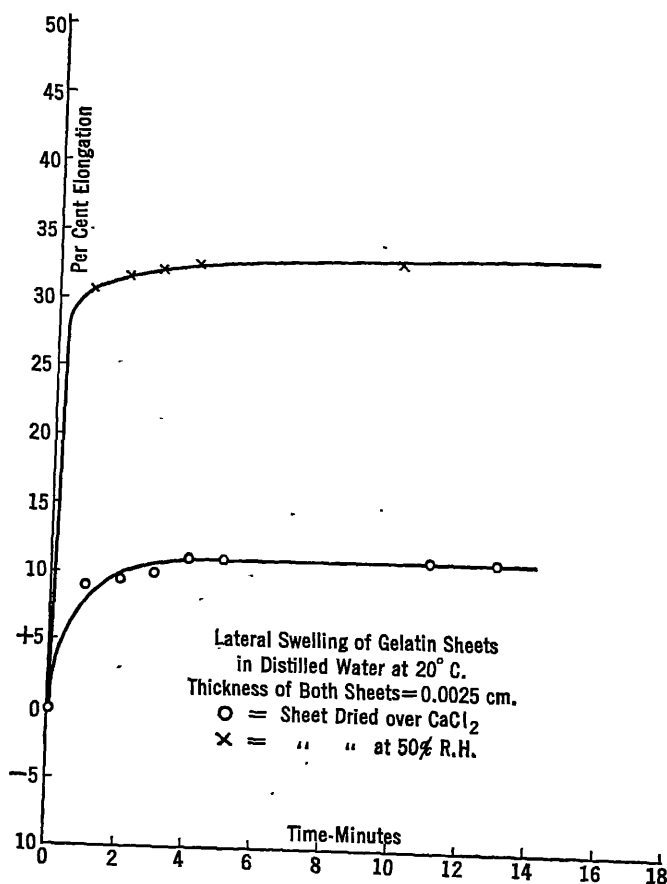


FIG. 17.

greatest area. But this is precisely the same condition as in a uniformly stretched in the plane of its largest surface, and dried. the strain so produced to persist after drying, and influence the water absorption as it manifestly does, it appears that a definite structure must be induced. Two major possibilities present themselves, *viz.*, (1) deformation of symmetrical (spherical) particles to elongated, flat-shaped particles; (2) orientation of preexisting asymmetric particles.

We consider it probable that the chief part of the residual strain is due to the latter arrangement, *viz.*, to reorientation of pre-existing rod- or tablet-shaped micelles or molecules.<sup>13</sup> Further evidence for this is brought out by the optical examination of gelatin sheets.

### THE BIREFRINGENCE OF GELATIN FILMS

Birefringence in gelatin jellies has been studied by Bjerken<sup>14</sup> and by Leick<sup>15</sup> and by Hatschek.<sup>16</sup> The birefringence of sheared gelatin solutions has been also extensively investigated by Kundt,<sup>17</sup> Umlauf,<sup>18</sup> and particularly by Hill.<sup>19</sup> Very little is recorded, however, for the case of dried gelatin films or sheets. Investigation of these was made with a special type of polarization microscope previously described in connection with the examination of the birefringence of films of cellulose esters.<sup>20</sup> A brief description will assist, however, in the understanding of the present results. A photograph of the completed instrument is given in Fig. 18 and the optical system is indicated in Fig. 19.

Light from the source *B* is collimated by the lens, *L*<sub>1</sub>. The specimen to be examined, *S*, is placed between the polarizing and analyzing nicols, *N*<sub>1</sub> and *N*<sub>2</sub>, and viewed through the objective, *L*<sub>2</sub>, and the eyepiece, *L*<sub>3</sub>. The phase shift in the polarized light on transmission through the specimen is equalized by Babinet compensator, *C*, the cross-hair *X* being used as a reference mark for the zero reading of the Babinet. The birefringence of the film is proportional to the distance necessary to shift the Babinet from its zero point to make the black interference lines coincide with the cross-hair. This is measured on a scale on the compensator. By calibration with Na-light a scale reading of 589 divisions corresponds to a retardation of 589  $\mu$ , *i.e.*, one wave-length of Na-light.

The specimen can be rotated in all three dimensions. By rotating either the specimen holder, or the nicols and compensator, the birefringence may be measured at any angle to the plane of vibration of the incident light. The position of the specimen may be determined in

<sup>13</sup> If the *micelles* in concentrated solutions consist of approximately spherical aggregates of elongated or chain-like molecules, with axes at random, then the deformation may consist in both (1) and (2) simultaneously, *viz.*, flattening of spherical micelles, with reorientation of elongated molecules.

<sup>14</sup> Wied. Ann., **43**, 808 (1891).

<sup>15</sup> Ann. Physik, **319**, 139 (1924).

<sup>16</sup> Kolloid-Z., **35**, 67 (1924); **36**, 202 (1925).

<sup>17</sup> Ann. Physik, **13**, 110 (1881).

<sup>18</sup> Ann. Physik, **45**, 304 (1892).

<sup>19</sup> Phil. Mag., **2**, (6) 524 (1901); **48**, (5) 485 (1899).

<sup>20</sup> McNally and Sheppard: J. Phys. Chem. (In press.)



relation to reference axes *A*, *B*, and *C*, as shown in Fig. 20 by the three circular scales shown in the photograph. Whenever a stretched film was examined, it was so placed in the holder that the direction of stretch coincided with the *B* axis.

The optical properties of a transparent colloid film can be determined by placing the film in the holder and reading the compensator for successive positions of the film rotated about the axes *A*, *B*, and *C*. The double refraction is plotted against the angle at which the measure-



FIG. 18.—Polariscope used for studying the double refraction of cellulosic films.

ment is made and the curve thus obtained compared with reference curves from sections of crystals of known symmetry.

The quantity  $\frac{\delta \cos \theta}{d}$  is taken as a measure of birefringence. Delta is the compensator reading when the film has been rotated  $\theta$  degrees from zero position, and  $d$  is the thickness of film in  $\mu$  mm. Hence  $\frac{\delta \cos \theta}{d}$  is the difference of path of the ordinary and the extraordinary ray in  $\mu$  per unit thickness of film. Using this instrument to control the optical properties, and applying a similar technic to that described in the paper

on cellulose ester films, we have prepared gelatin films of quite different optical and physical properties.

*Isotropic Gelatin Films.*—Isotropic gelatin films are very difficult to prepare, and we have not yet succeeded in forming a film isotropic over

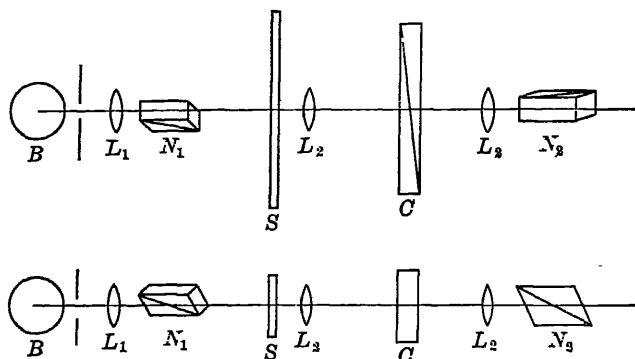


FIG. 19.

its whole area. Sufficient 5 per cent ash-free gelatin solution is poured on a mercury surface to cover an area about 4 cm. in diameter. To secure an isotropic film this must be dried very slowly.<sup>21</sup> Films dried rapidly show strong, irregular birefringence, particularly near the edges. The best specimens of isotropic gelatin films obtained required two weeks to

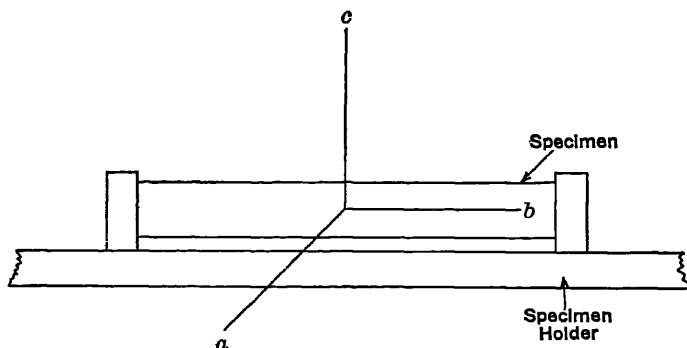


FIG. 20.

dry, and even these showed marked birefringence from the edge to about 1 cm. inward. The central portion was, however, quite isotropic, and it can be concluded that a *gelatin film dried on a mercury surface so that it is free to contract in all directions gives an isotropic film.*

<sup>21</sup> Cf. similar conditions for isometric drying of cubes of gelatin jelly, Sheppard and Elliott, *loc. cit.*

*Uniaxial Gelatin Films.*—Uniaxial gelatin films were formed by coating a gelatin solution on a nitrocellulose-coated plate. Table 1 gives the

TABLE 1.—DOUBLE REFRACTION OF PLATE-COATED GELATIN FILMS

(a) Sheet 61. Dried slowly at 65 per cent R.H. at 20° C.  $d = 0.042$  mm.

A Axis			B Axis		
$\theta$	$\delta$	$\frac{\delta \cos \theta}{d}$	$\theta$	$\delta$	$\frac{\delta \cos \theta}{d}$
0	0	0	0	0	0
10	0	0	10	0	0
20	-5	111	20	+2	44
30	-12	246	30	+10	205
40	-20	360	40	+20	362
50	-30	433	50	+30	457
60	-40	475	60	+40	475
350	0	0	350	0	0
340	-5	111	340	+2	44
330	-20	409	330	+10	205
320	-30	540	320	+20	362
310	-40	610	310	+27	411
300	-45	540	300	+38	452

Rotation about A axis;  $\theta = \text{any value}$ ,  $\delta = 0$ .

(b) Sheet 56. Dried rapidly at 30 per cent R.H. at 20° C.  $d = 0.05$  mm.

C Axis			B Axis		
$\theta$	$\delta$	$\frac{\delta \cos \theta}{d}$	$\theta$	$\delta$	$\frac{\delta \cos \theta}{d}$
0	0	0	0	0	0
10	-5	-98	10	0	0
20	-10	-186	20	+10	+186
30	-20	-344	30	+20	+344
40	-35	-532	40	+35	+532
50	-50	-640	50	+50	+640
60	-65	-650	60	.....	.....
350	-5	-98	350	0	0
340	-10	-186	340	+7	+130
330	-20	-344	330	+15	+258
320	-30	-532	320	+25	+380
310	-50	-640	310	+45	+570
300	-65	-650	300	.....	.....

Rotation about A axis;  $\theta = \text{any value}$ ,  $\delta = 0$ .

measurements made on films coated from the same 8 per cent solution of deashed gelatin, one of which was dried rapidly and the other slowly.

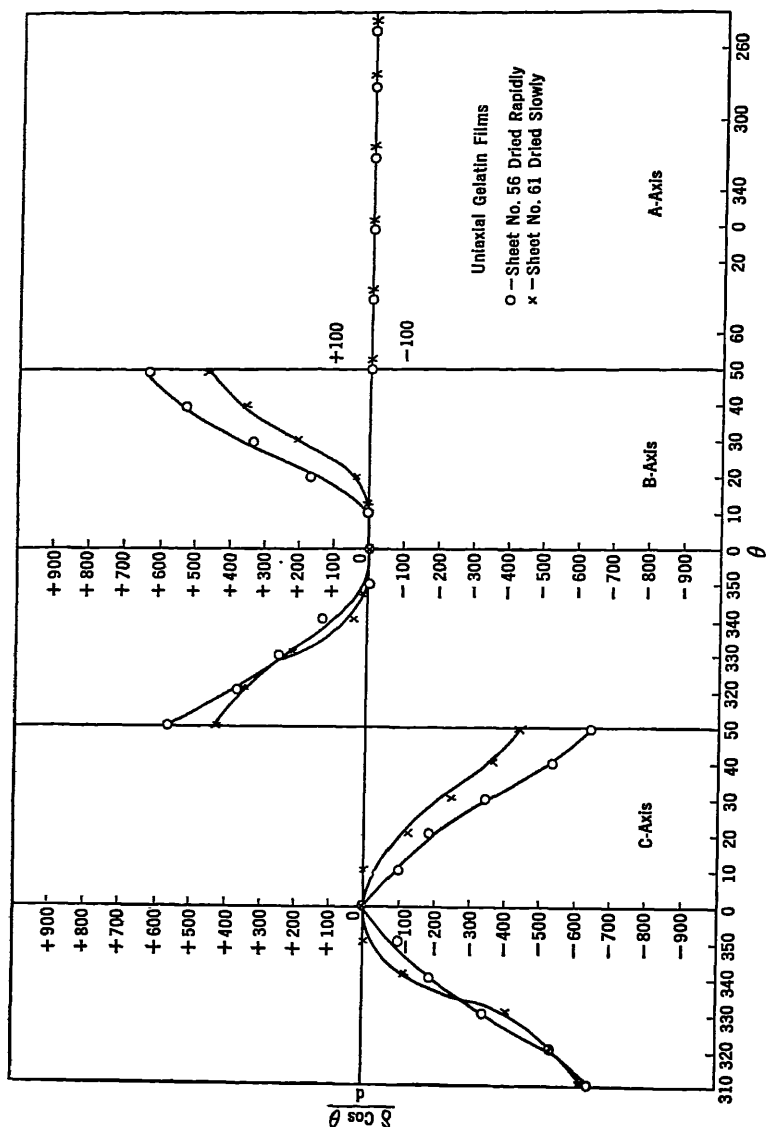


Fig. 21.

The curves in Fig. 21 are constructed from the data in the preceding table. There appears to be no well defined difference between the two gelatin sheets excepting, perhaps, a tendency for sheet 61 to show lower

values of double refraction at high angles. Whether or not this behavior is significant is not known.

*Biaxial Gelatin Films.*—An 8 per cent solution of de-ashed gelatin was coated and dried at 50 per cent R.H. to give a film 0.01 cm. thick. This sheet was then allowed to swell in distilled water at 23° C. for thirty minutes and then extended 20 per cent of its original length. The stretched film was dried without permitting contractions. Measurements of the double refraction of this gelatin film (No. 19) are given in Table 2.

TABLE 2.—DOUBLE REFRACTION OF STRETCHED GELATIN FILM No. 19

$$d = 0.11 \text{ mm.}$$

C Axis			B Axis			A Axis		
$\theta$	$\delta$	$\frac{\delta \cos \theta}{d}$	$\theta$	$\delta$	$\frac{\delta \cos \theta}{d}$	$\theta$	$\delta$	$\frac{\delta \cos \theta}{d}$
0	+55	+500	0	+ 55	+500	45	+55	500
10	+50	+445	10	+ 60	+540	25	+30	270
20	+40	+340	20	+ 70	+590	0	0	0
30	+30	+236	30	+ 85	+670	345	-30	-270
40	+15	+105	40	+100	+690	315	-55	-500
50	0	0	50	+140	+815	295	-30	-270
60	-20	- 91	60	.....	.....	270	0	0
350	+50	+445	350	+ 60	+540	250	+30	+270
340	+40	+340	340	+ 65	+550	225	+55	+500
330	+30	+236	330	+ 75	+590			
320	+15	+105	320	+ 90	+630			
310	-10	- 58	310	+105	+610			
300	-30	-135	300	+125	+570			

A second portion of the swollen gelatin sheet was stretched 38 per cent of its original length and dried at that elongation. Double refraction measurements on this sample (No. 18) are given in Table 3.

The curves in Fig. 22 are constructed from the data in the preceding Tables.

### GEL STRUCTURE AND ORIENTATION

It appears justifiable to conclude that the birefringence of these gelatin films is caused by the orientation of asymmetrical molecules or micelles by the forces set up in drying or stretching the jelly.

TABLE 3.—DOUBLE REFRACTION OF STRETCHED GELATIN, SHEET 18

C Axis			B Axis			A Axis		
$\theta$	$\delta$	$\frac{\cos \theta}{d}$	$\theta$	$\delta$	$\frac{\cos \theta}{d}$	$\theta$	$\delta$	$\frac{\cos \theta}{d}$
0	+100	+1030	0	+100	+1030	45	+100	+1030
10	+ 95	+ 960	10	+100	+1010	25	+ 85	+ 875
20	+ 90	+ 865	20	+105	+1010	0	0	0
30	+ 80	+ 705	30	+120	+1070	345	- 85	- 875
40	+ 70	+ 550	40	+140	+1100	315	-100	-1030
50	+ 50	+ 330	50	+160	+1070	295	- 85	- 875
60	+ 40	+ 206	60	+180	+ 930	270	0	0
350	+ 95	+ 960	350	+100	+1010	250	+ 85	+ 875
340	+ 90	+ 865	340	+105	+1010	225	+100	+1030
330	+ 80	+ 705	330	+120	+1070			
320	+ 70	+ 550	320	+140	+1100			
310	+ 50	+ 330	310	+160	+1070			
300	+ 40	+ 205	300	+180	+ 940			

The arrangement of the molecules or micelles may be roughly indicated by the diagrams in Fig. 23, in which (a) represents plan, side, and elevation of an isotropic film; (b) of a uniaxial film; (c) of a biaxial film.

It cannot be decided from these investigations whether the micelles in question are multimolecular, or are simply "macromolecules," *i.e.*, chain-like primary valence atom-groups, which the investigations of Meyer and Mark<sup>22</sup> no less than those of Staudinger<sup>23</sup> have shown to be the most probable fundamental entities of high molecular compounds such as cellulose and the proteins. The investigations in this laboratory<sup>24</sup> on the thickness of thin films of these bodies from dilute solutions show that the solution units from sufficiently dilute solutions must have one dimension of "low molecular" thickness. In the case of gelatin, a value for this molecular thickness of 7.0 Å.U. was obtained, in good agreement with the results of Gorter and Grendel.<sup>25</sup> We consider it probable, therefore, that such entities form the final structure units, but that in more concentrated solutions they are aggre-

<sup>22</sup> Ber., 61, 593 (1928).

<sup>23</sup> Ber., 61, 2427 (1928).

<sup>24</sup> Sheppard and Keenan: Nature, 121, 982 (1928); Keenan: J. Phys. Chem., 33, 371 (1929); Sheppard, Nietz, Keenan: Ind. Eng. Chem., 21, 126 (1929).

<sup>25</sup> Trans. Faraday Soc., 22, 477 (1926).

gated to multimolecular micelles, with very probable approach to nematic and smectic ordering in the micelles and "swarms."

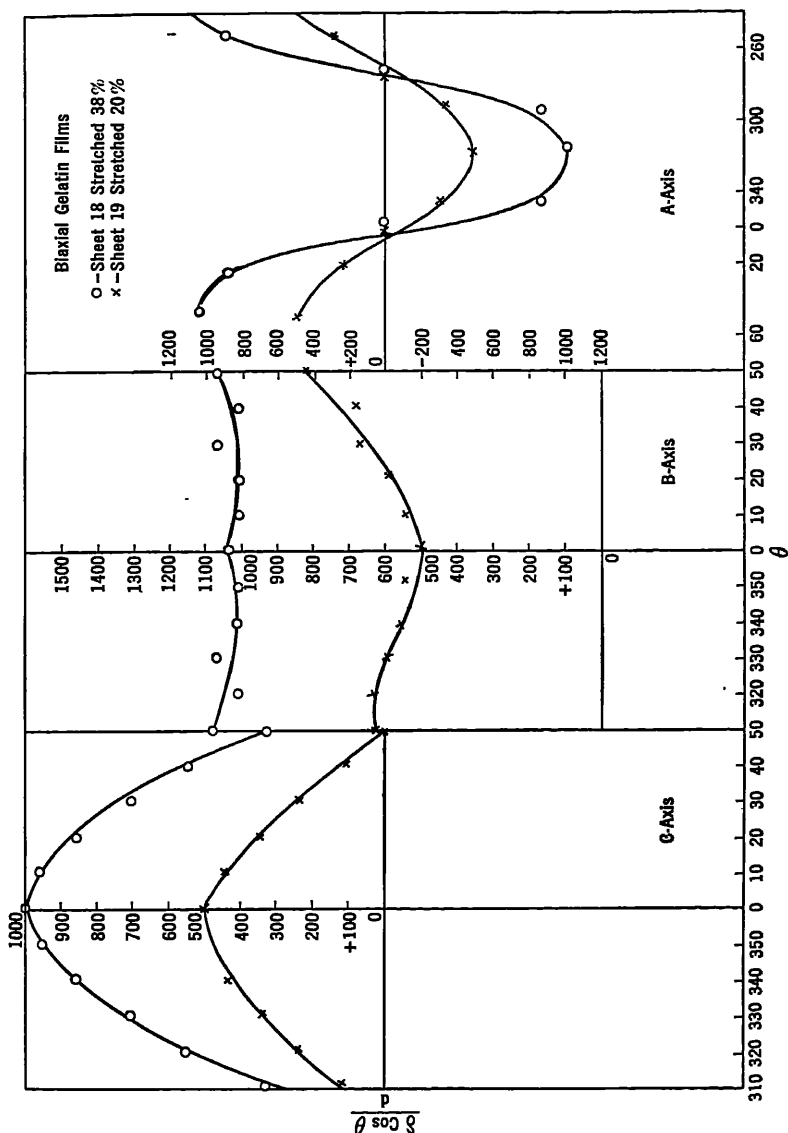


Fig. 22.

It was shown by Hatschek<sup>26</sup> that the optical anisotropy of gelatin jellies produced by stress does not decrease with mechanical relaxation

of the stress but remains, frequently, at the value corresponding to the first application of the stress. Hatschek has pointed out that this must be due to a permanent rearrangement of inner structure. This is in agreement with the view that gelation involves a condensation of ultimate molecular entities, which is followed by reorientation on application of stress.<sup>27</sup>

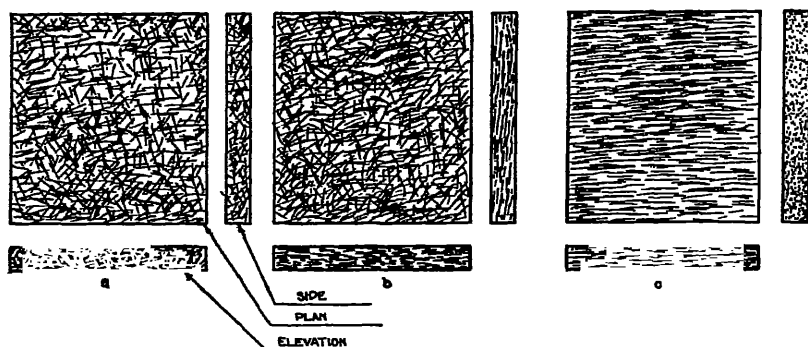
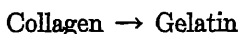


FIG. 23.—The arrangement of micelles in cellulosic films of different optical character, a, isotropic film; b, uniaxial film; c, biaxial film.

### GELATIN AND COLLAGEN

In terms of this hypothesis, the increase in optical anomaly obtained by stretching and drying gelatin jellies represents a movement in the direction of reversing the process:



Support for this conception is found from the very important observations of Katz and Gerngross<sup>28</sup> on the X-ray diffraction (powder) spectrum of collagen, gelatin, and strongly stretched gelatin, respectively. Applying the previous observation of Katz that strongly stretched rubber develops new "crystal interferences," they investigated other substances which like rubber develop heat on stretching, *i.e.*, show the Joule heat effect. In all such cases the development of heat may be referred to a recrystallization, or at any rate to the formation of a lattice-like ordering of molecule.<sup>29</sup> Gelatin jellies show this effect, and Katz and Gerngross succeeded in producing very considerable elongations—up to 400 per cent—of glycerin jellies of gelatin; from these the glycerin could be washed out and the tension maintained. Later a technic was

<sup>27</sup> See also Poole: *Trans. Faraday Soc.*, **21**, 82 (1926).

<sup>28</sup> *Naturwissenschaften*, **13**, 9001 (1925); *Kolloid-Z.*, **39**, 1801 (1926).

<sup>29</sup> Katz: *Loc. cit.*; Hock: *Kolloid-Z.*, **35**, 40 (1924).



developed for producing nearly as large elongations without the use of glycerin.

Dry unstretched gelatin gives a powder (Debye-Scherrer-Hull) diagram consisting of broad "amorphous" rings, and a sharp interference ring, similar to a crystalline interference. The inmost broad amorphous ring gives an identity period of 4 Å.U., and is followed outwardly by the sharp ring of period 2.7 Å.U. This is surrounded by a second "amorphous" band. The sharp band is obtained with pure ash-free gelatin. With the strongly stretched gelatin the bands developed intensity maximum for the direction of stretch, and with very strong gelatin a spectrum was developed *hardly distinguishable from that of collagen*.

The diagram of collagen is not a pronounced "point" or fiber diagram<sup>30</sup> and, as Katz and Gerngross point out, may represent a mesomorphic, *e.g.*, smectic state,<sup>31</sup> *i.e.*, bundles of similarly oriented elongated molecules, the bundles again repeating in the same direction, but with no lattice arrangement in the other dimensions. In view of the possibly "arborescent" character of the gelatin (or collagen) molecule,<sup>32</sup> it seems possible that the preferred direction is that of a main chain or trunk, and that the existence of side chains reduces the possibility of complete lattice development.

We consider that our results on the anisotropy of gelatin gels are entirely in harmony with the observations of Katz and Gerngross, and afford further evidence of the substantial identity of the ultimate gelatin and collagen molecules. With the progress of actual hydrolysis of the molecule, the capacity for reorientation becomes reduced; the scission fragments increase the proportion of amorphous material.

The relation of this conception to the observation of Northrop and Kunitz<sup>33</sup> on the swelling of isoelectric gelatin, and on the fractionation<sup>34</sup> of gelatin into "soluble" and "insoluble" portions we propose to discuss in a future paper. It is inviting to identify the "insoluble" portion with a regenerated collagen fraction, the "soluble" portion with hydrolytic scission fragments of the macromolecules, but consideration of this must await further experiments.

ROCHESTER, NEW YORK.

<sup>30</sup> Implying axial orientation of crystallites themselves having inner three-dimensional lattice formation.

<sup>31</sup> Friedel: *Ann. Physik*, **18**, 273 (1923).

<sup>32</sup> Sims: *J. Gen. Physiol.*, **11**, 629 (1928).

<sup>33</sup> *J. Gen. Physiol.*, **8**, 317 (1925-28); **10**, 102 (1926-27); Kunitz: *Ibid.*, **10**, 811 (1926-27); **12**, 289 (1928).

<sup>34</sup> Kunitz and Northrop: *J. Gen. Physiol.*, **12**, 379 (1929).



# THE MEASUREMENT OF THE HYDRATION OF GELATIN AND SIMILAR MATERIALS AND THE RELATION OF HYDRATION TO SWELLING

BY HARVEY A. NEVILLE AND EDWIN R. THEIS

## I. PRINCIPLES

THE terms *hydration* and *swelling* have been largely confused or used synonymously with reference to the effects which obtain when gelatin, hide substances, or similar materials are permitted to soak in water or aqueous solutions. *Swelling* is evaluated by measuring the final increase in volume or weight of a definite quantity of a material when it is immersed in a liquid. The effect of variation in hydrogen-ion concentration upon the magnitude of the swelling of gelatin was investigated by Loeb, who obtained the now familiar swelling curve showing a minimum swelling at the isoelectric point of the gelatin (pH 4.7). It has been assumed by most authors that hydration parallels swelling and that hydration will hence likewise exhibit a minimum at pH 4.7. By an application of the Donnan theory of membrane equilibrium, Procter and Wilson<sup>1</sup> have furnished a very satisfactory theory of the mechanism of swelling. This theory accounts for the effect of variation in pH upon the degree of swelling as represented in the curve obtained by Loeb.

According to the Procter-Wilson theory, the entrance of water and hence the increase in volume of a solid block of gelatin is caused by osmotic force due to a difference in total concentrations of diffusible ions inside and outside the gelatin. However, as pointed out by Loeb, at the isoelectric point gelatin is practically not ionized and there can be no Donnan equilibrium. Yet when dry grains of isoelectric gelatin are placed in water of pH 4.7 a considerable swelling occurs. With regard to this, Loeb continues<sup>2</sup>: "The swelling (at the isoelectric point) must be determined by forces different from those set up by the Donnan equilibrium. In the first place, there are those forces of chemical attraction between the molecules of water and certain of the groups of the gelatin molecule which cause the solution of gelatin in water when the

<sup>1</sup> J. Chem. Soc., 109, 307 (1916).

<sup>2</sup> "Proteins and the Theory of Colloidal Behavior," New York, McGraw-Hill Book Co., 193 (1922).

forces of cohesion between the gelatin molecules forming the gel can be overcome. The absorption of water by dry grains of isoelectric gelatin at pH 4.7 is, therefore, primarily but in all probability not exclusively due to the residual valency forces, and the swelling of solid isoelectric gelatin granules is primarily a phenomenon of solid solution."

This factor to which the swelling at the isoelectric point is attributed must also be present and active to a greater or less extent at other pH values and must be responsible for a part of the total swelling obtained under these other conditions. This absorption of water due to residual valences or the hydrophilic nature of the material we have called *hydration*. It is the purpose of this paper to show how this factor may be measured, how it changes under varying conditions, and to indicate the relation of this hydration factor to the total swelling of the material.

## II. METHOD

It has been noted in many investigations of swelling that although the material which is swelling increases in volume, the system as a whole undergoes a contraction. This fact has not been taken into consideration in the various attempts to explain swelling. It is neglected, for example, in the Procter-Wilson theory since the observed contraction of the system can not be explained as due to the transfer of solvent by osmotic force. In other words, the study of swelling has been limited to a consideration of the changes in volume or weight of the solid phase. It seems that the measurement of the net volume change of the whole system under varying conditions might likewise give results of considerable importance.

The apparatus illustrated in Fig. 1 was designed for this purpose. It is essentially a simple dilatometer, consisting of a bottle with a ground-glass stopper through which is sealed a calibrated capillary tube. The ground-glass connection is lubricated with stop-cock grease and will hold without leaking even under a considerable hydrostatic pressure. However, heavy rubber bands attached to the neck of

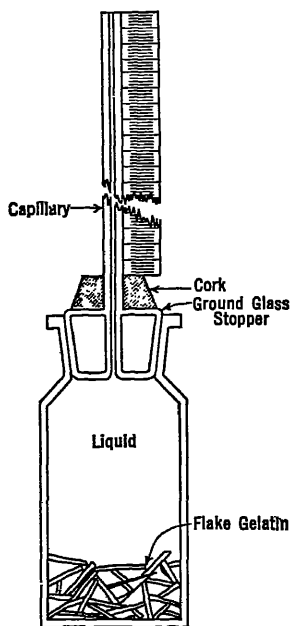


FIG. 1.—Apparatus for measuring the volume change of the system.

the bottle may be pulled over the cork cushion in order to insure a tight joint.

The volume of the bottle is 150 cc., and in most of the experiments 20 gm. of gelatin in flake form were used. However, it is interesting to note that within the range 5 to 20 gm. of gelatin the contraction observed is directly proportional to the quantity of gelatin present. Because of the simplicity and compactness of the apparatus a number of them were used concurrently in the same thermostat in order to obtain checks or to observe the effects with different solutions under identical external conditions.

The apparatus and all materials were always brought to a uniform temperature in a thermostat before each experiment. The materials were then quickly transferred to the bottle part of the apparatus, any air bubbles were removed, and when the stopper was inserted the liquid rose in the capillary to a height which served as the origin for subsequent readings. The apparatus was kept immersed in the thermostat during the experiment, the position of the liquid in the calibrated capillary was noted at intervals, and this gave a direct measure of the changes in volume of the system.

A similar apparatus was described by Neville and Jones<sup>3</sup> for the study of the hydration and setting of plaster of Paris and Portland cement. The analogy of these processes to the hydration of gelatin was pointed out in that paper.

The hydration or addition of water to colloids is ascribed by Pauli<sup>4</sup> to the formation of a highly compressed liquid shell about the particles. Such a phenomenon must be accompanied by an increase in density which indicates a compression of the medium (water) or a compression of the particle by its water layer. Hence a contraction of the system gelatin-water must indicate hydration, and measurement of this contraction under varying conditions must give a relative measure of the hydration of the hydrophilic material. From such measurements of this contraction the actual compression may be calculated approximately. Our results indicate that it is of the order of 1000 atmospheres per gram of gelatin in 150 cc. of water at 0° C.

Svedberg<sup>5</sup> attempted to show from density measurements that the degree of hydration of gelatin in solution paralleled the viscosity changes as observed by Loeb, giving a minimum at pH 4.7 and a maximum at about pH 3. This relation is not necessarily true since the viscosity of

<sup>3</sup> "Colloid Symposium Monograph," 6, 309 (1928).

<sup>4</sup> "Colloid Chemistry of the Proteins," P. Blakiston's Son & Co., Philadelphia, 10 (1922).

<sup>5</sup> J. Am. Chem. Soc., 45, 2613 (1923).

gelatin solutions depends upon the electro-viscous effect as well as upon the degree of hydration of the particles. The method of calculation used by Svedberg was shown to be erroneous by Brown.<sup>6</sup>

In a later paper Svedberg<sup>7</sup> published some data obtained by a volume-change method, and these results, so far as they go, are in agreement with ours. Svedberg found that the presence of acids, bases and salts decreases the contraction of the system; that there is no change in hydration when a gelatin sol sets to a gel; that hydration increases with decreasing temperature.

### III. RESULTS

In Fig. 2 are shown typical curves which represent the volume decrease of the system gelatin-water with time. These results were

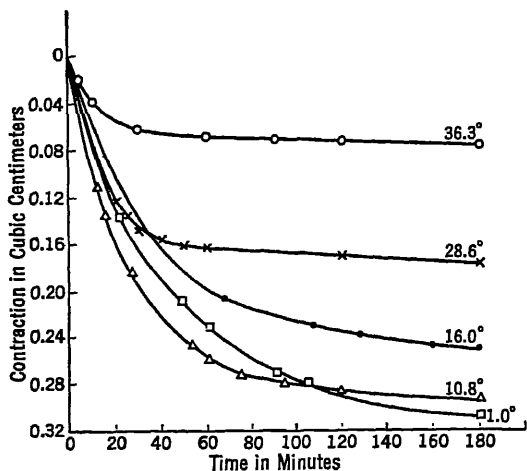


FIG. 2.—The contraction of the system gelatin-water at various temperatures.

obtained with 20 gm. of bone gelatin in flake form in freshly-boiled, distilled water. The pH value of the supernatant liquid at equilibrium was 6.3. Each curve represents the volume change at the temperature indicated, and two features are evident. First, the final contraction of the system and hence the degree of hydration increases as the temperature is decreased; second, the rate at which equilibrium is attained is much greater at the higher temperatures. Thus, at 36.3° C. very little change is observed after the first thirty minutes, while at the lowest temperature, 1° C., 3 hours are required to reach equilibrium. Both of the effects just noted are characteristic of adsorption phenomena. The change in the degree of hydration of this gelatin with temperature is illustrated in Fig. 3 where the equilibrium contraction of the system gelatin-water is shown as a function of temperature.

<sup>6</sup> J. Am. Chem. Soc., **46**, 1207 (1924).

<sup>7</sup> J. Am. Chem. Soc., **46**, 2673 (1924).

This relation is in striking contrast to the influence of temperature upon swelling. Since osmotic pressure is proportional to absolute temperature, the osmotic force which, according to the Procter-Wilson theory, causes swelling must increase with increasing temperature. Hence swelling increases with temperature and, in the case of gelatin, when the osmotic force causing the entrance of water into the gelatin structure exceeds the cohesive strength of the gelatin, the gelatin goes into solution. This usually occurs at temperatures above  $30^{\circ}\text{C}$ . The regularity of the curve in Fig. 3 supports the statement of Svedberg that there is no observable change in hydration between the gel and sol states of gelatin.

As already stated, it was found by Svedberg that the presence of electrolytes decreases the degree of hydration of gelatin. On the other hand, electrolytes may either increase or decrease the degree of swelling, depending upon whether they increase or decrease the disparity in total

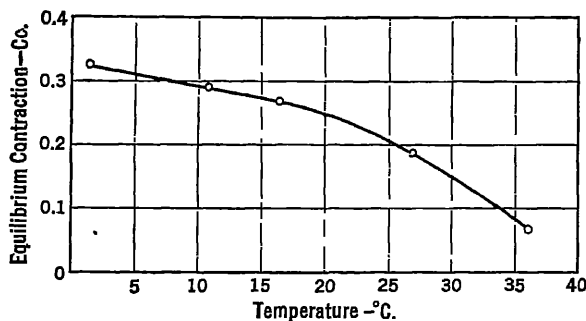


FIG. 3.—The relation of the hydration of gelatin to temperature.

concentrations of diffusible ions inside and outside the gelatin structure. We have measured the contraction which occurs when flake gelatin is permitted to soak in solutions of HCl and NaOH over a considerable range of  $p\text{H}$  values. The data represented in Fig. 4 are the contractions observed after three hours, at which time equilibrium has been attained. The  $p\text{H}$  value in each case is that of the solution in equilibrium and was obtained by pouring off the supernatant liquid and mixing it. A sample of this was taken and the  $p\text{H}$  value determined by means of the Youden quinhydrone electrode. Salts such as NaCl likewise decrease the contraction, giving much smaller volume changes than would correspond to the point on the curve in Fig. 4 if  $p\text{H}$  value were the only important factor.

If gelatin exhibits maximum hydration at or near its isoelectric point, it should be possible to effect dehydration by placing fully hydrated gelatin in a solution which is considerably more acid or basic. Dehydra-

tion may be pictured as a decrease in the compression of the water envelope of the particles. This should result in an expansion of the system and a rise in the capillary of our apparatus. This is exactly

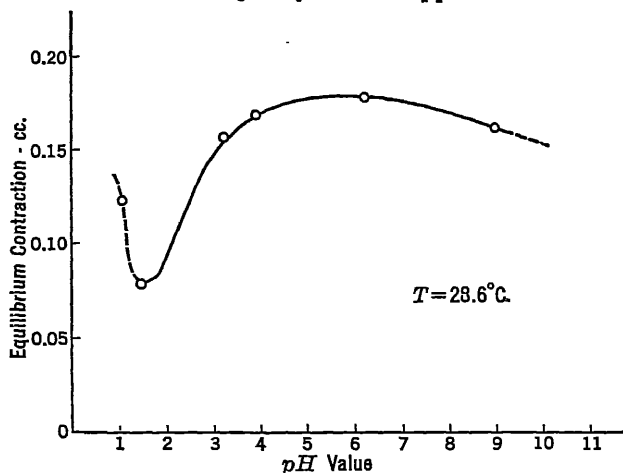


FIG. 4.—The relation of pH value to the contraction of the system gelatin-water, or hydration.

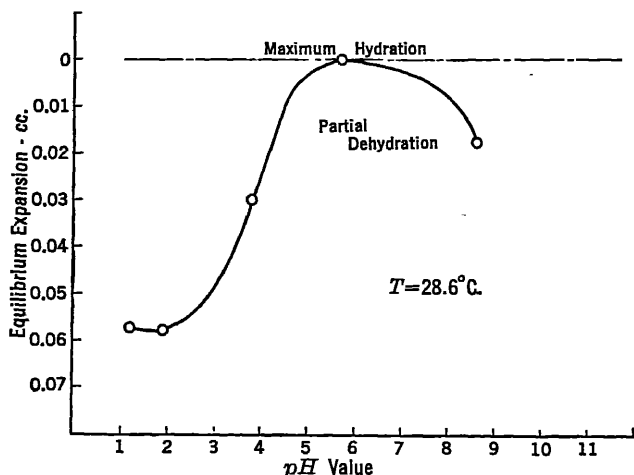


FIG. 5.—The relation of pH value to the expansion of the system gelatin gel-solution, or dehydration.

what is observed when blocks of a 10 per cent gelatin jelly are placed in solutions of electrolytes. When such pieces of gelatin jelly are placed in distilled water there is no observable change in the volume of the system. This indicates that the gelatin in such condition is fully



hydrated. The results with solutions of HCl and NaOH are represented in Fig. 5. The striking similarity of the curves in Figs. 4 and 5 show that we are dealing with an equilibrium condition which may be approached from either side.

#### IV. DISCUSSION AND SOME APPLICATIONS

If we may assume that the swelling of isoelectric gelatin in an isoelectric solution is due solely to hydration, then we may superimpose, as in Fig. 6, the swelling curve of Loeb upon the hydration curve shown in Figs. 4 and 5 and thus contrast the influence of pH value upon each. Many authors have stated that swelling is always accompanied by a decrease in the volume of the system. That this is not necessarily true

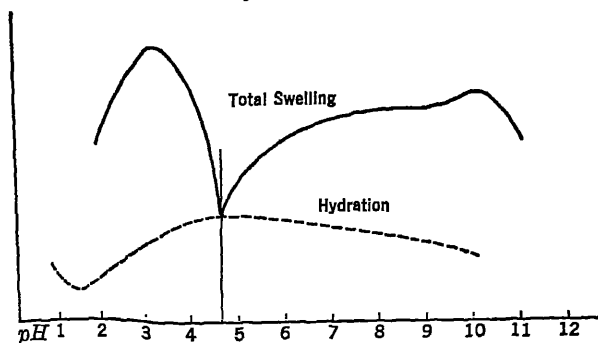


FIG. 6.—The relation of hydration to total swelling, and the influence of pH value upon each.

can be shown by a simple experiment and is illustrated in Fig. 6. If we permit gelatin to hydrate and swell at pH 4.7 and then transfer this swollen and hydrated material to a solution of pH 3, the material will swell further as can be measured by its increase in weight or volume, but in this case the volume of the whole system will also increase due to the dehydrating effect of the increased acid concentration. That is, swelling will follow the upper curve in Fig. 6 which represents the volume or weight change of the solid phase alone, while the change in volume of the system as a whole follows the lower curve, the expansion resulting in a condition of less compression or contraction. Here we have a case of swelling accompanied by an *increase* in the volume of the system. Since swelling may be accompanied by either an increase or a decrease in the volume of the system it seems probable that the two effects are largely independent and that the volume change of the system is due to other factors, an important one of which is the compression of the medium by the adsorptive forces of the hydrophilic material.

While we have assumed, as in Fig. 6, that at or near the isoelectric point hydration is the only factor causing a contraction in the volume of the system, there are particularly at lower and higher pH values most probably other influences which have not yet been evaluated but which may affect the volume change of the system. The increase in the final contraction shown in Fig. 4 for pH values less than 1.5 must be due to such factors. At this high concentration of acid the original nature of the gelatin may be changed by hydrolysis or other chemical action. Such action may be accompanied by a volume change or a modified gelatin with a different hydration capacity may be produced.

The volume-change method described above for the study of gelatin has also been applied by the writers to animal skin in the form of corium and cured hide. One paper on this phase has already been published<sup>8</sup> in which it was shown that the soaking and liming processes could be controlled conveniently by this method. Degenerative changes, presumably due to bacterial action and resulting in destruction of leather substance, show up on our apparatus as an expansion following a latent bacterial period during which normal contraction occurs. In the case of poorly cured domestic hides this expansion begins after six hours when the hide is soaked in water or very dilute acids, while for South American hides a longer soaking period, in some cases thirty-six hours, may be used before bacterial action sets in. It was suggested that liming should be started on any batch of hides at that point of maximum hydration before bacterial action becomes dominant.

With regard to the soaking of hides, leather technologists distinguish two effects which they call *swelling* and *plumping*. It is suggested that swelling corresponds approximately to what we have called hydration, that water taken up by the osmotic swelling is mechanically held and is largely lost when the hide goes through the wringers, but water of hydration, since its addition is accompanied by a contraction in the volume of the system, can not be removed by the application of pressure.

The results shown in Fig. 5 which indicate the expansion of the system occurring when a fully hydrated material is placed in electrolytes, suggested that the action of substances which are considered *astringent* might be studied by this means. In Fig. 7 are shown the results obtained when 20 gm. samples of cured hide which had been soaked twenty-four hours and limed five days were placed in solutions of recognized astringent action. Similar results may be obtained by using pieces of a 10 per cent gelatin jelly as was done in obtaining the results shown in Fig. 5. Since there is no standard method of evaluating the astringency of various solutions, it may be that this volume-expansion method may prove of

<sup>8</sup> Theis and Neville: Ind. Eng. Chem., **21**, 377 (1929).

value in giving a relative measure of this property and in setting up definite standards. On the basis of results presented in this paper it appears that the action of an astringent is the dehydration of tissues, causing them to contract and thereby also forcing out some of the mechanically held water of swelling.

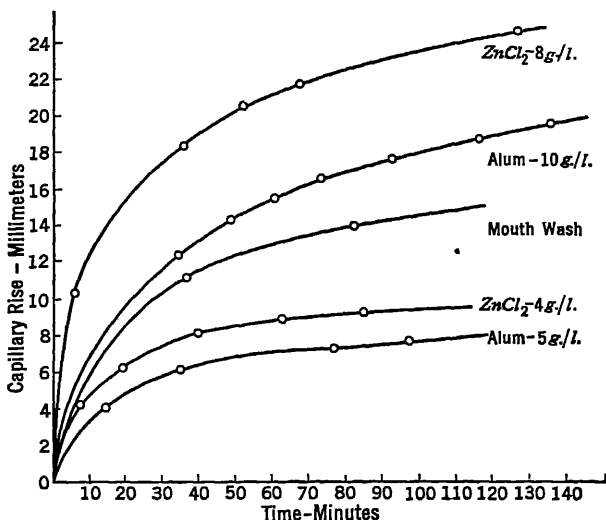


FIG. 7.—The dehydrating effect of astringents upon limed hide.

### SUMMARY

1. A method is devised to measure the change in the volume of the system when gelatin and similar materials are permitted to hydrate and swell in water or solutions.

2. The swelling of gelatin at the isoelectric point can not be due to osmotic force but may be attributed to hydration—that is, to the compression of a shell of liquid about the particles which results in a contraction of the system.

3. The variation of this volume change with change in temperature and pH value is measured and is contrasted with the changes in osmotic swelling under the same conditions.

4. The application of this method to the soaking of animal skins is indicated and the probable relation of plumping and swelling is suggested.

5. When fully hydrated hide or gelatin is placed in an astringent solution, an expansion of the system results. The measurement of this expansion may serve as a method of determining relative astringency of various solutions.

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# THE INFLUENCE OF ADSORPTION ON THE GROWTH OF CRYSTAL SURFACES

BY KARL F. HERZFELD

## I. INTRODUCTION

THE influence of impurities ("companions") on the formation and growth of crystals has long been known. Tammann<sup>1</sup> has investigated this influence on the formation of new crystalline centers in the molten substance and on the velocity of growth.<sup>2</sup> The influence of companions on the external form (habit) of crystals is well known<sup>3</sup> and has been ascribed to adsorption of the companion modifying the rate of growth of the different surfaces of the crystal.<sup>4</sup> Dr. Hettich and myself have studied the influence of impurities on etching figures.<sup>5</sup> Quite recently, Saylor<sup>6</sup> has described a new method to measure the difference of adsorption for different crystal faces and Frazer<sup>7</sup> has developed in this University an optical method to determine adsorption on an area of less than 1 sq. mm.

The following brief discussion may be considered as one means of theoretical approach.

## II. THE INFLUENCE OF ADSORPTION ON THE SURFACE TENSION

We call  $n$  the number of molecules of the impurity adsorbed on 1 sq. cm. of the surface,  $N$  the number of available places (number of adsorbed molecules at saturation),  $c$  the concentration of the companion in solution. Then we have according to Gibbs<sup>8</sup> for the surface tension  $\sigma$

$$-n = \frac{c}{KT} \frac{d\sigma}{dc} \quad (1)$$

<sup>1</sup> See, e.g., Tammann: *Aggregatzustände*, Leipzig, 226 (1922).

<sup>2</sup> Loc. cit.

<sup>3</sup> E.g., Spangenberg: *Z. Krist.*, **59**, 375 (1924); Gille and Spangenberg: *Z. Krist.*, **65**, 204 (1927).

<sup>4</sup> Marc and Wenk: *Z. physik. Chem.*, **68**, 104 (1909); Marc: *Z. physik. Chem.*, **73**, 685 (1910); **79**, 71 (1912).

<sup>5</sup> Herzfeld and Hettich: *Z. Physik.*, **38**, 1 (1926); Hettich: *Z. Krist.*, **64**, 265 (1926); Honess: "Etch Figures," New York (1927).

<sup>6</sup> Saylor: *Colloid Symposium Monograph*, **5**, 192 (1927).

<sup>7</sup> *Phys. Rev.*, **33**, 97 (1929).

<sup>8</sup> "Collected Papers," New York, **1**, 232, 235 (1928).

We use now for  $n$  Langmuir's equation<sup>9</sup> ( $a$  a constant)

$$n = N \frac{ac}{1 + ac} \quad (2)$$

and find

$$\sigma_0 - \sigma = NKT \ln(1 + ac) \quad (3)$$

which equation is similar to an empirical equation of Szyszkowski.<sup>10</sup>

For small adsorbed amounts, far from saturation, we get

$$\sigma_0 - \sigma = NKT ac = nKT \quad (3')$$

As  $N$  is in a monomolecular layer at best  $\frac{1}{(3.10^{-8})^2} = 10^{15}$  and more probably  $10^{14}$ , we find in this case  $\sigma_0 - \sigma < 40$  ergs/sq. cm., more probably  $< 4$  ergs/sq. cm. If we introduce a concentration  $c' = \frac{1}{a}$ , at which half the surface is covered by adsorbed molecules,

$$n = N \frac{ac'}{1 + ac'} = \frac{N}{2} \quad (4)$$

we can rewrite (3)

$$\sigma_0 - \sigma = NKT \ln\left(1 + \frac{c}{c'}\right) \quad (3'')$$

It follows then that for large adsorption  $\sigma_0 - \sigma$  increases above the limit given above, but rather slowly. For a concentration  $10^6$  times as high as the one which would give half saturation, a concentration at which only  $10^{-6}$  of the surface would remain free,  $\sigma_0 - \sigma$  would be  $6.2, 30 \sim 14$  times the above limit, that is,  $\sigma_0 - \sigma \sim 560$  ergs/sq. cm. or rather 56 ergs/sq. cm.

The free surface energy of the crystal is then, if the index  $s$  characterizes the  $s$ -th surface of area  $\omega_s$

$$F = \sum_s \left[ \sigma_0^{(s)} - N^{(s)} KT \ln\left(1 + \frac{c}{c'_s}\right) \right] \omega_s \quad (5)$$

### III. INFLUENCE ON THE FORMATION OF CENTERS OF CRYSTALLIZATION

As Gibbs<sup>11</sup> has shown, the vapor pressure of a drop of liquid or the solubility of a small crystal is increased (its melting point decreased) on account of its surface tension. This is the reason for the possibility of

<sup>9</sup> J. Am. Chem. Soc., **38**, 2221 (1916).

<sup>10</sup> Z. physik. Chem., **64**, 385 (1908).

<sup>11</sup> Loc. cit. p. 229

oversaturation, as at first small crystal centers have to be formed, which have a higher free energy and accordingly a higher solubility (*e.g.*) than corresponds to the concentration of a saturated solution which would be in equilibrium with a large crystal. That any centers at all are formed for a given small oversaturation in spite of the fact that they have to start as very small centers which would be in equilibrium only with a much higher concentration, can be accounted for by the presence of fluctuations. Volmer<sup>12</sup> has recently given a very interesting quantitative theory of this which calculates the number of centers of given size present at a certain concentration. Farkas finds, that at a certain concentration  $c$  above saturation the number of nuclei which go on growing produced per second is

$$Z = \frac{cC}{\rho A} \sqrt{\frac{2\sigma N_a M}{\pi}} e^{-\frac{A\sigma}{3RT}} \quad (6)$$

Here  $\rho$  is the density,  $M$  the molecular weight,  $N_a$  the Avogadro number,  $A$  the surface of the critical particle

$$A = 2\pi \left( \frac{4\sigma M}{\rho RT \ln \frac{c}{c_{sat}}} \right)^2 \quad (7)$$

and  $C$  a constant of the order of magnitude of  $cN_a$ . This formula holds for isotropic spheres, but we are going to apply it here too, as the exact calculations for crystals are too complicated and the small centers can probably be treated approximately as spheres. As Volmer has pointed out, the  $Z$  is rather sensitive to  $\sigma$ . If accordingly for the pure substance there appears at a certain concentration a sufficient number of centers to term the process crystallization, a decrease in  $\sigma$  will greatly increase this number. While it is possible to estimate the surface tension of some crystals against vacuum, leading to values around 100–200 ergs/sq. cm. for alkali halides, no values are available for the tension between a crystal and its molten phase or between a crystal and an aqueous solution, but one would estimate it to be much lower, the latter on account of the attraction between water and a salt (if one takes a crystal out of the solution, the water is torn asunder, not torn from the crystal leaving it dry), the first, at least for organic crystals, on account of the small difference between the forces in the crystal and the molten phase (low heat of fusion). The change of  $\sigma$  by adsorption of impurities (decrease of  $\sigma$  by a large fraction) should therefore result in an increase of the

<sup>12</sup> Volmer and Weber: *Z. physik. Chem.*, **119**, 277 (1926); Volmer: *Z. physik. Chem.*, **125**, 151 (1927); Farkas: *Z. physik. Chem.*, **125**, 236 (1927).

number of centers. This has been found in some cases by Tammann (molten betol with benzamide or anisic acid as impurities). The interesting question arises whether so much can be adsorbed that  $\sigma$  becomes negative. In general, one might expect that if the attraction of the crystal for the impurity is so great, it will form a solid solution instead of accumulating in high concentration on the surface only. But assuming it does so, small crystal centers would be present even below saturation concentration or above the melting point and would start to grow to large crystals immediately upon reaching the saturation point. This is possible only if so little impurity is present that most of it is taken out of the solution by the formation of a few centers, otherwise we would have the formation of lather or gel below actual saturation. Perhaps such a case is present in the experiments of Othmer,<sup>13</sup> who found the number of centers formed per second greatly decreased after heating the molten substance for some time above the melting point. If we have there an impurity which lessens  $\sigma$  sufficiently to form permanent centers, these might be destroyed by long heating to higher temperature and might take a long time to reform, as formation of the center and subsequent adsorption to make it stable must occur.

Finally also negative adsorption is possible, with

$$\sigma - \sigma_0 \sim RT\delta \qquad \delta \sim 10^{-7} \text{ cm}$$

which would diminish the number of centers, as is the case with molten betol and naphthalin as impurity.

#### IV HABIT OF CRYSTALS

##### (a) EQUILIBRIUM

The question whether the external form of crystals is the form of minimum surface energy<sup>14</sup> has been answered negatively<sup>15 16</sup> for macroscopic crystals, as the differences in solubility are too small and experiments<sup>16 17</sup> have confirmed this by showing no change of form in saturated solution. But for microscopic crystals this will be different and one could expect in equilibrium the form of smallest surface energy. Experiments on this point will be started here next year. But in this

<sup>12</sup> Curie: Bull. soc. franc. mineral., 8, 145 (1855); Wulff: Z. Krist., 34, 512 (1901).

<sup>13</sup> Othmer: Z. anorg. Chem., 91, 209 (1915).

<sup>15</sup> Gibbs: Loc. cit., p. 325.

<sup>16</sup> Valetton: Ber. Sachs. Ges. Wiss., 67, 37 (1915); Z. Krist., 60, 31 (1924).

<sup>17</sup> Neuhaus: Z. Krist., 68, 15 (1928).



case the condition in the presence of an adsorbed impurity is not any more

$$\Sigma \sigma_0^{(s)} \delta \omega_s = 0$$

but

$$\Sigma \left[ \sigma_0^{(s)} - KTN^{(s)} \ln \left( 1 + \frac{c}{c'_s} \right) \right] \delta \omega_s = 0 \quad (8)$$

From the numbers given in II it follows then that for a salt crystal growing in its vapor, the adsorption of an impurity present in moderate amount will not be able to change the equilibrium form greatly, but for a crystal in solution or for organic crystals the differences in the surface tensions are probably smaller and can perhaps be overcompensated by adsorption.

For large crystals, the influence of impurities must act upon the velocity of growth. A new theory of the growth of heteropolar salts has been recently developed by Kossel.<sup>18</sup> He compares in a lattice of rock-salt type the energy gains, if an ion is attached to a smooth surface of the cube, to a straight step formed by a half-finished lattice plane lying on top of another and, finally, if attached to a corner formed by a half-finished row, the rows being the elements which build up a plane. He finds that the energy amount greatly increases in this order. Accordingly he explains the normal appearance of cubes in this manner: Assume that we already have a partly finished row, forming part of a plane. Then the next ion is most likely to be attached (or if attached, most likely to stay) at the unfinished part of the row, and so gradually the row is completed. When the row is finished, it is impossible to gain as much energy as during the completion of the row, but the most probable place for a new ion will be in a step, adjacent to the row just finished, and so a new row will be started. In this manner, the lattice plane will be completed. When the plane has, in its upbuild, reached the border of the cube (the border of the underlying plane), a new plane has to be started. At all places available now for a new ion it will be held very much less tightly than in any of the places during the construction of the preceding plane, and accordingly the starting of each new plane will mean some delay. But among all the places now available the corners will be the ones with the highest attraction because the number of surrounding ions of the same sign, which give repulsion, is smallest. So a new row will start at a corner, then a new plane will be built up systematically, resulting in a cube.

This is in general agreement with the geometric theory of crystal

<sup>18</sup> Quantentheorie Chem., Leipzig, 1 (1928); see, also, Gibbs: *Loc. cit.*, p. 325.

growth,<sup>19</sup> according to which the most prominent surfaces of a crystal are the ones having the slowest growth in the direction of their normal. The small probability of an ion being fixed on a completed plane, as developed by Kossel,<sup>20</sup> means namely a very slow growth normal to the surface of the cube (100), the moderate speed of formation of a new row a moderate speed of growth of the surface of a rhombododecaeder (110), the highest probability being the attachment of an ion in a corner formed by an incomplete row, which corresponds to a high speed of growth of an octaeder-surface (111).

The same principles will now apply also to the explanation of the influence of adsorbed companions. Any companions, the adsorption of which is due to specific electric forces and not to van der Waals forces in general, especially ions or dipole substances and substances with active groups, will be adsorbed much stronger in corners or steps than on the plane surfaces<sup>19 21</sup> for the same reason given above for the strong attachment of the ions belonging to the crystal itself. In other words, these places form the active spots of Taylor.<sup>22</sup>

But in this case, the adsorbed molecules cover the surface of the octaeder completely, preventing the structural elements of the crystal from being attached to the surface and cutting down the rapid growth.<sup>23</sup> They will cut down also somewhat the growth of the surface of the cube, because they will occupy some of the positions at the corners from which the growth of the cube-surfaces starts. But as they are not very strongly adsorbed there, this diminution will not be strong. Actually, the recent measurements of Neuhaus<sup>24</sup> have proved that the appearance of octahedric forms of rock salt growing in a solution containing urea is due to the fact that, while both the rate of growth of (100) and (111) is diminished, the diminution for (111) (octaeder) is so much greater that the order of the two is reversed.

If the adsorption is rather strong, so that all the places of rapid growth are practically covered, the growth apparently stops completely.<sup>25</sup> This is due to the very large differences in the rate of growth,

<sup>19</sup> Johnsen: "Wachstum und Auflösung der Kristalle," Leipzig (1910); Gross: Abh. Sachs. Ges. Wiss., **35**, 137 (1918).

<sup>20</sup> Kossel: Gott. Nachr., July 29, 135 (1927); Lennard-Jones and Dent: Trans. Faraday Soc., **24**, 92 (1928); Bluh and Stark: Z. Physik., **43**, 575 (1927); Stranski: Z. physik. Chem., **136**, 259 (1928).

<sup>21</sup> Schwab and Pietsch: Chem.-Ztg., **53**, 392 (1929).

<sup>22</sup> Taylor: Colloid Symposium Monograph, **4**, 19 (1926).

<sup>23</sup> It is clear that this adsorption might go parallel with a formation of complexes in the solution. E. g. Spangenberg: Z. Krist., **59**, 375 (1924); Gille and Spangenberg: Z. Krist., **65**, 204 (1927).

<sup>24</sup> Neuhaus: Z. Krist., **68**, 15 (1928).

the surfaces left free growing very slowly. On the other hand, the rate of dissolution is not or not very strongly diminished by adsorption.<sup>25</sup> This is easily explained, as the process of breaking loose an ion is not intrinsically different whether the ion borders directly on the solution or is covered with an adsorbed molecule. A moderate diminution might result either from an attachment of the adsorbed molecule to more than one ion<sup>26</sup> in which case it would form an additional link, or from a very large size of the adsorbed molecule preventing the solvent from breaking immediately into the gaps between the departing ion and the underlying crystal.

This relatively small difference must be responsible for the appearance<sup>27</sup> of etch-hills on dissolving crystals in the presence of impurities, the smallness being manifest in the relatively short life of these figures.

<sup>25</sup> Marc and Wenk: *Z. physik. Chem.*, **68**, 104 (1909); Marc: *Z. physik. Chem.*, **73**, 685 (1910); **79**, 71 (1912).

<sup>26</sup> Burk: *J. Phys. Chem.*, **32**, 1601 (1928).

<sup>27</sup> Herzfeld and Hettich: *Z. Physik.*, **38**, 1 (1926); Hettich: *Z. Krist.*, **64**, 265 (1926); Honess: "Etch Figures," New York (1927).

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# CRYSTAL STRUCTURE AND ADSORPTION FROM SOLUTION

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## I.

THE crystalline form of matter has been the object of interest and study from the earliest times, and a large number of efforts have been made to determine the exact nature of crystallographic phenomena. Early workers, such as Huygens (1629-1695) and Rene Haüy (1743-1882), made remarkable contributions, many of which now constitute an important part of modern crystallography. However, the results of the last twenty years indicate that it is doubtful if the early workers fully realized with what complicated phenomena they were dealing. We are just now beginning to correlate the structure of the crystal with its growth and polyhedral form.

The investigations of the last century on crystal growth fall into three main divisions. First, the work of the nineteenth century dealing with the effects produced upon the crystal form or color by the variation of external conditions. Second, the investigations centering around the Noyes-Whitney and Nernst diffusion theories of crystal growth. Finally, the contributions since 1917, which correlate our recent knowledge of the ultimate structure of the crystal with its growth forms.

The application of X-ray methods of crystal analysis to the study of adsorption and catalysis has led to valuable results. The powder method of X-ray analysis has been extended to colloid systems by Scherrer,<sup>2</sup> Haber,<sup>3</sup> and others. Scherrer established the identity of the crystal lattices of colloiddally dispersed gold and macrocrystalline gold. Haber<sup>3</sup> found that the particles of a zinc sulfide sol also possess a crystal-

<sup>1</sup> The material used in this article is taken largely from the Doctor's dissertations produced in the writer's laboratory by Drs. J. D. McBurney (1924), T. S. Eckert (1925), F. G. Keenen (1926), G. W. Bennett (1927), and M. E. Lash (1928), together with the Master's dissertation of Mr. A. H. Burkholder (1929). A part of this work has appeared in the following Journal articles: France and McBurney: *J. Am. Chem. Soc.*, **46**, 540-44 (1924); Eckert and France: *J. Am. Cer. Soc.*, **10**, 579-91 (1927); Keenen and France: *Ibid.*, 821-27; Bennett and France: *J. Am. Cer. Soc.*, **11**, 571-81 (1928); France: *Colloid Symposium Monograph*, **3**, 317 (1926).

<sup>2</sup> Scherrer: *Nachr. Ges. Wiss. Göttingen*, 96 (1918).

<sup>3</sup> Haber: *Ber.*, **55B**, 1730 (1922).

line structure. Similar results have been obtained by others. Investigations of this kind should prove helpful in solving the various problems concerned with the stability of suspensoid systems. If it is true that the dispersed particles of a suspensoid system are in reality minute crystals of colloidal dimensions, then one should expect the crystallographic forces, present during the growth of the crystal, to be influential in limiting the size of the particles and the stability of the system. This would be especially true in the case of those systems prepared by condensation methods, where the presence of such forces would be effective in bringing about an adsorption of various matter from the solutions used. Since the majority of suspensoid systems are prepared in this way, it was thought desirable to study the relation of the structure of a crystal to the adsorption effects resulting from the growth of the crystal in the presence of matter foreign to the crystal. It was with these ideas in mind that the work, herein presented, on the relation of the crystal structure to the adsorption of foreign substances by the different crystal planes was undertaken.

It has long been known that crystals may be colored when grown in the presence of dyes and many studies of such phenomena have been made. A partial outline of the work closely related to the present problem follows:

Senarmont<sup>4</sup> appears to have been the first to observe such effects. He found that strontium nitrate pentahydrate was noticeably colored by saffranine, turmeric and ammoniacal logwood. The crystals were found to be dichroic, and in addition, had undergone changes in crystalline form.

Following Senarmont, work predominately qualitative in character was continued by several investigators.<sup>5</sup> A large part of the contributions of Gaubert was qualitative.<sup>6</sup> However, he<sup>7</sup> crystallized phthalic acid from seventeen different dye solutions, and measured the weight of dye taken up by the crystals, using a colorimetric method. He found

<sup>4</sup> Ann. chim. phys., (3) 41, 319 (1854); Compt. rend., 38, 101 (1854).

<sup>5</sup> Scherr-Thoss: Wied., 6, 284 (1879); Kny: Ber. deut. botan. Ges., 5, 394 (1887); Lehman: Z. Krist., 12, 391 (1887); 22, 609 (1894); 27, 438 (1897); Z. physik. Chem., 8, 543 (1891); Wied. Ann., 51, 47 (1894); Ann. Physik., (4) 2, 682 (1900); 8, 908 (1902); Becquerel: Ann. chim. phys., (6) 14, 249 (1888); Ambrohn: Ber. deut. botan. Ges., 7, 113 (1889); Pellikan: Tschermak's mineral petrog. Mitt., 13, 258 (1892); Retgers: Z. physik. Chem., 12, 600 (1893); Z. Krist., 25, 512 (1896); Maschke and Vater: Z. Krist., 33, 57 (1900).

<sup>6</sup> Gaubert: Bull. soc. franc. mineral, 17, 121 (1894); 23, 211 (1900); 28, 180 (1905); Compt. rend., 151, 1134 (1910); 155, 649 (1912).

<sup>7</sup> Gaubert: Bull. soc. franc. mineral, 28, 286 (1905); Compt. rend., 142, 219 (1906).

this weight to be practically the same for all dyes, and further was unable to detect any change in the interfacial angles, density or the melting point of the crystals.

Marc, and Marc and Wenk<sup>8</sup> in their studies of crystallization and solution velocities, observed that dyes retarded the crystallization velocity but not the solution velocity of crystals. From this they concluded that the equilibrium between crystal and dye in saturated solution is not kinetic in character. Marc measured the adsorption of dyes by such substances as barium sulfate, barium carbonate, calcium sulfate, uric acid, lead sulfite, and magnesium carbonate by stirring the powdered material through the dye solution, and found that the adsorption isotherm was followed. Under these conditions it is doubtful if we are dealing with the same phenomenon as when growing crystals are used.

Reinders<sup>9</sup> crystallized silver chloride in the presence of dyes by blowing air through an ammoniacal solution of silver chloride, thus removing the ammonia and causing the silver halide to precipitate. He found 22 dyes that colored the crystals but only 5 of them caused a modification of the crystal habit. Reinders ascribed the failure of the 17 dyes to modify the crystal habit to their low concentration in the crystals. Colorimetric measurements of the weight of dye taken up by the crystals were made. In the case of erythrosin, which did not change the crystal habit, this weight was independent of the crystallization velocity, and in the case of rose bengal which modified the habit, the concentration of the dye in the crystals was independent of its concentration in the solution.

Paneth and his coworkers<sup>10</sup> studied the adsorption of ponceau 2R, methylene blue B extra, methyl green and naphthol yellow by various crystalline powders such as lead sulfate, lead sulfide, lead chromate and barium sulfate by stirring the crystals through solutions of the dyes. They believed the dye to be adsorbed as a monomolecular layer. In the case of ponceau 2R on lead sulfate it was thought that 31 per cent of the surface was covered by the dye.

Walton and his students<sup>11</sup> have investigated the velocity of crystallization of undercooled water and aqueous solutions. Their method closely resembled that used by other investigators working with under-

<sup>8</sup> Marc and Wenk: *Z. physik. Chem.*, **68**, 104 (1910); Marc: *Z. physik. Chem.*, **73**, 685 (1910); **75**, 710 (1911); **79**, 71 (1912).

<sup>9</sup> *Z. physik. Chem.*, **77**, 677 (1911).

<sup>10</sup> Paneth and Vorwerk: *Z. physik. Chem.*, **101**, 480 (1922); Paneth and Thiman: *Ber.*, **57**, 1215 (1924); Paneth and Radu: *Ber.*, **57**, 1221 (1924).

<sup>11</sup> Walton and Judd: *J. Phys. Chem.*, **18**, 717 (1914); **18**, 722 (1914); Walton and Brann: *J. Am. Chem. Soc.*, **38**, 1161 (1916); **38**, 317, (1916); Brann: *J. Am. Chem. Soc.*, **40**, 1168 (1918).

cooled melts. Crystallization was induced in a long L-shaped tube previously filled with water and undercooled to a definite temperature. The progress of crystallization up the tube could be accurately followed and timed with a watch, and in this way the rate of crystallization determined. Experiments were conducted in which the effect of various chlorides, nitrates and sulfates upon the velocity of crystallization was investigated. Their results showed that those substances which were most highly hydrated produced the greatest decrease in the velocity of crystallization. Experiments with various organic compounds and substances of high molecular weight such as gelatin, agar, sugar and starch indicated that the solvation of the dissolved substance was the main factor in the decreasing of the velocity of crystallization. Brann<sup>12</sup> working with formamide in a like manner concluded that solvation was the essential feature causing the decreased velocity of crystallization of this substance.

In the quantitative study of dye adsorption by crystals, most of the work has been done on adsorption by insoluble powders and not by the crystal during its growth. It has been shown that the adsorption of dyes on crystalline powders probably occurs as a monomolecular layer but it is extremely unlikely that the same condition obtains when a crystal is allowed to grow in a solution containing dye.

It has been shown in this laboratory<sup>13</sup> that when basic lead carbonate is electrolytically precipitated in the presence of gelatin both the crystal form and the uniformity of the particle size of the resulting precipitate are greatly modified. The particle size is reduced and the uniformity coefficient is increased. Working with dye solutions of copper sulfate from which crystals were grown it was found<sup>14</sup> that quinoline yellow, methylene blue and bismarck brown decreased the growth rate of copper sulfate. It was believed that these effects were due to the adsorption of the foreign materials by the crystal at the crystal solution interface. The adsorption was thought to be the result of the interaction of the polar groups in the adsorbed material and the electrical force fields of the crystal.

This work made it evident that if any relation existing between the crystal structure and the adsorption of foreign materials was to be found certain very definite experimental conditions would have to be met. These conditions are: (1) The use of crystalline substances whose crystal lattices are known; (2) the use of foreign materials (ions, molecules or groups) of known structure; (3) the selection of some crystallographic

<sup>12</sup> J. Am. Chem. Soc., 40, 1184 (1918).

<sup>13</sup> France and McBurney: *loc. cit.*

<sup>14</sup> Eckert and France: *loc. cit.*



constant that could be accurately measured and that would change as adsorption occurred; (4) the use of a single macroscopic crystal freely suspended in the solution uninfluenced by the presence of other crystals. This is an important consideration since it has been shown that when a number of crystals are growing in one another's presence the rate of growth of each is not equal.

The third condition was met by the measurement of growth ratios. Thus in the alum crystal shown in Fig. 1 (A) the ratio of the increase in the perpendicular distance between parallel cube faces (100) and the increase in the perpendicular distance between parallel octahedral faces (111) during any given time interval is a constant and characteristic value for any normally growing crystal. Any change in this value means that the rate of growth (perpendicular displacement) of one pair of faces has been altered to a greater extent than that of the other pair. Since it is known that the adsorption of materials by crystal faces results in a repression of the face displacement, then the measurement of this ratio should afford a simple means of determining whether a given substance is adsorbed to a greater extent at one face than at another. The first, second, and fourth conditions were met by the use of single macroscopic crystals of potassium, ammonium, and cesium, alums, and lead nitrate grown in the presence of various foreign materials including amino acids, dyes and gelatin.

An automatic photographic method was used to obtain the growth record. A well-formed crystal was suspended from a platinum wire in a saturated solution contained in a glass cell having plane parallel sides. The crystal was so oriented that two pairs of faces were in sharp focus on

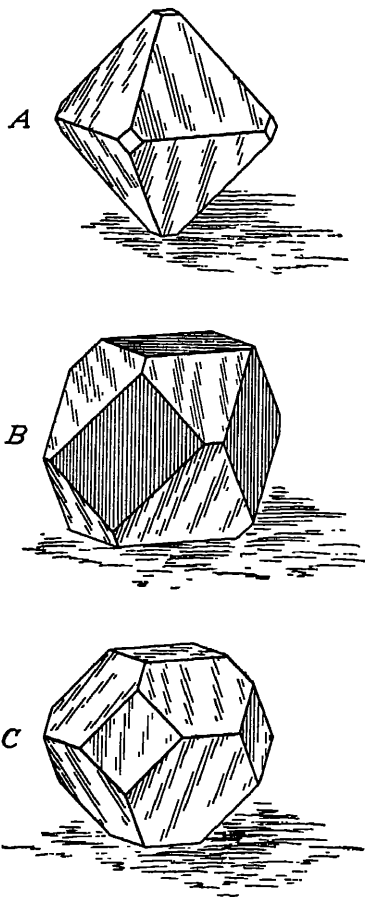


FIG. 1.—Diagrams of potassium alum crystals.

the film of a motion picture camera when a beam of light was passed through the cell. Growth took place as the solution evaporated at constant temperature and exposures were made at half-hour intervals. After a growth period of from twelve to thirty-six hours the film was removed from the camera and developed. The measurement of the successive face displacements was made from the projected images of the film at a magnification of about  $25\times$ .

Figure 2 is a diagrammatic arrangement of the apparatus used. It consists of a large air thermostat and three mechanical units: (1) the thermal regulator; (2) the illuminating and optical system; and (3)

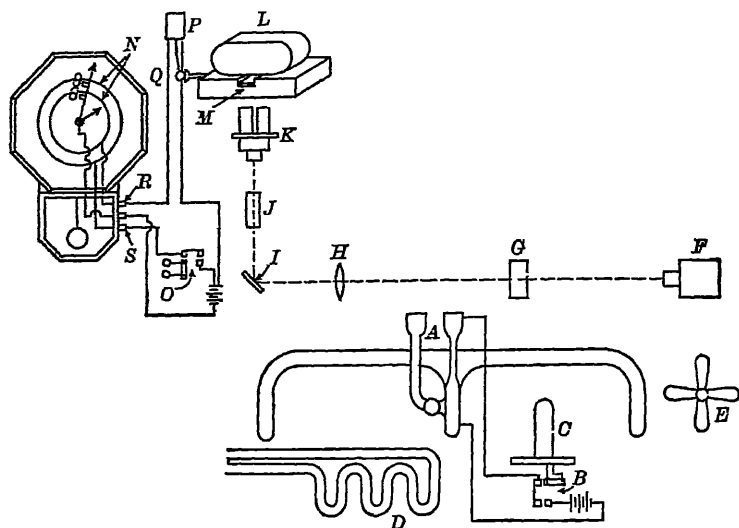


FIG. 2.—Schematic arrangement of apparatus for recording crystal growth.

the automatic mechanism controlling the camera and illuminating system.

The thermostat which contains the thermal and optical units, is a box, 3 by 6 by 6 ft., made of "compoboard" on a wood frame, covered with du Pont "fabricoid" and equipped with two sliding observation windows which may be removed when access to the thermostat is desired. Temperature variations did not exceed  $\pm 0.1^\circ$  (at  $30.0^\circ$  C.), and under favorable circumstances were not over  $\pm 0.05^\circ$ , over 24-hr. periods.

A shelf bearing the optical unit divides the thermostat in two parts. Beneath the shelf is the thermal unit. Two liters of toluene contained in a large U-shaped glass tube (A, Fig. 12), 9 ft. long, by its expansion and contraction causes mercury to make and break an electrical circuit.

This mercury makes and breaks contact through a battery of 6 dry cells, operates a relay, *B*, which in turn makes and breaks contact from the 110-volt a.c. line. The temperature is maintained by a standard Mazda 250-watt, 110-volt heater lamp, *C*. A water-cooling coil of copper tubing, *D*, serves to equalize temperatures, while a small fan, *E*, provides thorough air circulation.

The illumination and optical unit is made up as follows: Light from a Bausch & Lomb microscope lamp, *F*, equipped with a 108-watt lamp, passes through the crystallization chamber, *G*, then through a projection lens, *H* (Bausch & Lomb 6 E.F.), and is reflected at right angles by a plane mirror, *I*. A telephoto lens, *J* (Dallmeyer, London,  $F = 4$  in.), directs the beam into a binocular eyepiece, *K*, provided with 5-mm. lenses. One ocular of this eyepiece focuses directly on the film in a Bell & Howell automatic spring-driven motion picture camera, *L*, from which the lens is removed. This type of camera uses 16-mm. kodak safety film and is set in motion by simply depressing a small button which releases the motor that drives the film and operates the shutter. The action continues as long as the release button is depressed. The other ocular focuses on a ground-glass plate, *M*, which is at exactly the same level as the film in the camera. The crystal is thus kept in focus at all times without disturbing the camera. Focusing is done entirely by adjusting the projection lens which is provided with a screw for this purpose.

The automatic mechanism which is outside the thermostat is controlled by a specially modified eight-day clock. Beneath the face of the clock are two concentric brass rings, *N*, insulated from each other and from the clock face, each of which is wired to a corresponding binding post on the outside of the clock cabinet. Two concentric circles of holes lined up radially at five-minute intervals in the outer edge of the face of the clock permit removable brass plugs, insulated from the clock face, to be screwed into these brass rings. A silver minute hand bears at right angles to its end two strips of spring bronze, the under sides of which are covered with a tough, fibrous, insulating sheeting. This insulating material reaches to within a few millimeters of the ends of the bronze strips, and is slightly shorter on one of them. The minute hand makes good electrical contact with the works of the clock which are wired to a third external binding post. The minute hand after passing over the brass plugs causes the bronze strips to make contact with them. This hand is high enough to pass over the plugs without itself touching them and the hour hand is shortened so as not to interfere with the movement of the the bronze strips.

Two circuits pass through the clock by means of the common binding

post; one to a relay, and one to a single stroke bell mechanism. The strip having the longer metallic surface makes contact with its corresponding plug before the second strip makes contact. The first circuit closed, operates the relay, *O*, by means of a battery of 6 dry cells. When the relay closes, the 110-volt a.c. line passes through the transformer which operates the Bausch & Lomb illuminating lamp. Shortly after this lamp has reached its maximum intensity, the second shorter bronze strip makes contact. The same battery of dry cells used on the thermal regulator operates a single stroke bell mechanism, *P*, from which the gong has been removed. The clapper, *Q*, of this bell communicates its thrust to a rod which rests against the camera release button. Five seconds later the minute hand has carried the bronze strips past the plugs and both circuits are broken. The bell clapper has a slight "kick" past its resting position when the current is on, and it is this kick which, when the communicating rod is of just the right length, makes the taking of a single exposure possible by only momentarily depressing the release button. If, however, it is desired to make two or three exposures, the rod is lengthened a little, thereby increasing the time the release button is depressed. Of course, it is also possible to take the pictures as long as the current passes through the bell mechanism, by making the rod still longer. The removable plugs permit variations in the time interval between single exposures of from five to thirty minutes and one hour. By placing strips on the hour hand and adding another pair of concentric rings, other time intervals could be had.

*Potassium Alum.* Potassium alum crystals were grown from solutions containing methyl violet, bismarck brown, diamine sky blue, methylene blue, quinoline yellow, naphthol yellow, ponceau red, picric acid, and gelatin. Of these dyes only bismarck brown and diamine sky blue colored the crystal and modified its habit. Gelatin was also without effect except in such high concentration that the gel state was almost reached. Table 1 contains a summary of the measured ratios. The mean value  $V_{100}/V_{111} = 1.61$  for the pure alum is smaller than that obtained by Valetton<sup>15</sup> but since he used spheres as starting points rather than crystals already in their normal polyhedral form, the two cases are not strictly comparable.

It is evident that with bismarck brown and diamine sky blue the rate of growth of the cube faces along the normal to their surfaces is retarded to a greater extent than that of the octahedral. Especially striking is the case of diamine sky blue in which a concentration of 0.01 per cent actually stopped the growth of the (100) faces without affecting that of the (111) faces.

<sup>15</sup> Z. Krist., 59, 335-65 (1923).

TABLE 1.—RESUME OF TABLES I-XXII\*

POTASSIUM ALUM

Sample	Substance	Per Cent	$V_{100}/V_{111}$	Mean
I	Pure alum.....	0.0	1.50	
II	Pure alum.....		1.49	
III	Pure alum.....		1.67	
IV	Pure alum.....		1.80	1.61
V	Pure alum.....		1.58	
VI	Pure alum.....		1.66	
VII (a)	Naphthol yellow.....	0.01	1.56	1.62
VII (b)	Naphthol yellow.....	0.01	1.68	
III (a)	Quinoline yellow.....	0.01	1.55	1.59
III (b)	Quinoline yellow.....	0.01	1.63	
IX (a)	Methylene blue.....	Less than 0.01	1.69	1.66
IX (b)	Methylene blue.....	Less than 0.01	1.63	
X (a)	Methyl violet.....	Less than 0.01	1.62	
X (b)	Picric acid.....	0.01	1.71	1.71
XII (a)	Bismarck brown F.....	0.0012	1.27	1.24
XII (b)	Bismarck brown F.....	0.0012	1.21	
XIII (a)	Bismarck brown F.....	0.0025	1.10	1.14
XIII (b)	Bismarck brown F.....	0.0025	1.15	
IV (a)	Bismarck brown F.....	0.0050	0.70	0.70
IV (b)	Bismarck brown F.....	0.0050	0.70	
XV (a)	Bismarck brown F.....	0.0100	0.64	0.63
XV (b)	Bismarck brown F.....	0.0100	0.62	
IV	Gelatin.....	0.50	1.50	
VII	Gelatin.....	1.00	1.57	
III	Gelatin.....	2.00	1.24	
IX	Diamine sky blue FF.....	0.01	$V_{100} = 0$	
XX	Diamine sky blue FF.....	0.005	0.28	
XI	Diamine sky blue FF.....	0.003	1.37	
XII	Diamine sky blue FF.....	0.001	1.14	

\* See Keenen and France: J. Am. Ceram. Soc. 10, 821 (1927)

The facts noted are illustrated by Fig. 1 in which *A* is a drawing of a pure alum crystal, *B* that of one grown in 0.01 per cent diamine sky blue, and *C* one grown in 0.01 per cent bismarck brown. *C* was colored brown throughout, and it is evident that a decrease in the  $V_{100}/V_{111}$  ratio is accompanied by an increase in the areas of the (100) faces. This represents the appearance of having only the (100) faces colored deep blue, indicated by the shading on the cube faces in the drawing, while the (111) are perfectly clear. This seems without doubt to show clearly that a dye may be selectively adsorbed by certain crystal faces, and in consequence the perpendicular rates of growth are altered, thereby

changing the shape of the crystal. Continued growth in this dye yields perfect cubes of alum, colored blue on all 6 faces.

The curves, I and II, for bismarck brown and diamine sky blue, respectively, of Fig. 3 show the effect of increasing concentration of dye on the ratios. These curves tend to flatten out at the higher concentrations.

The crystal structure assigned to the alums by Vegard and Schjelderup,<sup>16</sup> Wyckoff,<sup>17</sup> and Valetton,<sup>18</sup> while they differ in some respects all show that the cube faces have alternating planes of  $\text{Al}^{+++}$  and  $\text{K}^+$  ions in one plane and  $\text{SO}_4^{--}$  in the next. The octahedral faces possess a checker board arrangement of the above ions.

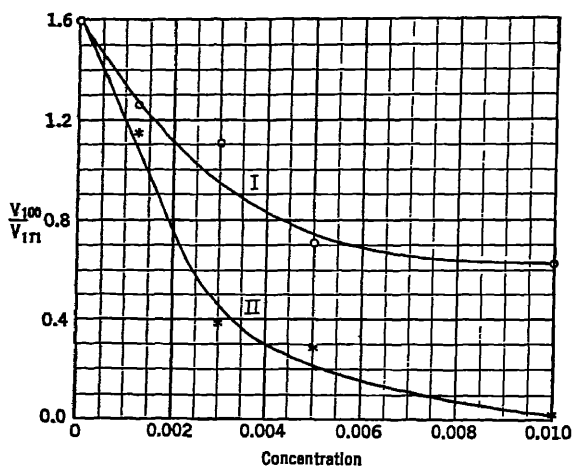


FIG. 3.—Growth ratio-concentration curves for potassium alum.

I = Bismarck brown;

II = Diamine sky blue.

This structure has been employed by Spangenberg<sup>19</sup> to explain the relative rates of growth of the octahedral and cube faces of potassium alum. Applying these structural relations to the adsorption of the foreign substances by the alum one would expect the adsorption to be greater at the cube faces than at the octahedral. Confirmation of this is observed in the cases of bismarck brown and diamine sky blue, both of which are exclusively adsorbed by the cube faces. These results strongly suggest that the structure of the crystal is a factor in the adsorption process as the dyes were adsorbed only at the cube faces,

<sup>16</sup> Ann. Physik., (4) 54, 146 (1917).

<sup>17</sup> Z. Krist., 57, 595 (1923).

<sup>18</sup> Z. Krist., 56, 434 (1921).

<sup>19</sup> Z. Krist., 61, 189 (1925).

these being the ones having the stronger fields. It is apparent, however, that the ionic structure of the crystal face is not the only factor in the adsorption process, since many of the substances were not adsorbed at all. Doubtless the physical and chemical character of the adsorbed material is of equal importance. In this connection the presence and distribution of polar groups within the molecule are significant. Such variations in the adsorbed materials may account for the differences in the quantitative effect of the bismarck brown and the diamine sky blue in repressing the cube face displacement. The latter dye was between two and three times as effective as the former. No doubt the interionic distances within the crystal together with the magnitude of the force fields extending out from the crystal faces and also from the dye molecules are important factors which should be considered.

*Ammonium Alum.* This alum has the same structure as the potassium alum except for the substitution of the  $\text{NH}_4^+$  ion for the  $\text{K}^+$  ion. From the results obtained with potassium alum one would predict adsorption to take place at the cube faces and the growth ratio  $V_{100}/V_{111}$  to be reduced to a lower value than that for the normal alum. Table 2

TABLE 2.—EFFECT OF FOREIGN SUBSTANCES ON CRYSTAL HABIT OF AMMONIUM ALUM

Bismarck brown.....	No effect	Fuch sine.....	No effect
Methylene blue.....	No effect	Flavazine.....	No effect
Naphthol yellow.....	No effect	Methyl violet.....	No effect
Brilliant green.....	No effect	Victoria scarlet.....	No effect
Ponceau red 2R.....	No effect	Pararosaniline base.....	No effect
Quinoline yellow.....	No effect	Saffranine.....	No effect
<hr/>			
Congo red.....	Insoluble in alum solution		
Immedial green.....	Insoluble in alum solution		
Thiocarbonyl.....	Insoluble in alum solution		
Diamine sky blue FF.....	Repressed cube faces		
Oxamine blue B.....	Repressed cube faces		
Anthraquinone green.....	Repressed cube faces		
Crystal violet.....	Colored crystal throughout without affecting growth ratio		
Gelatin.....	No effect		
Agar-agar.....	No effect		
Asparagine.....	No effect		
Phenylaminoacetic acid.....	No effect		
Five per cent formalin.....	No effect		

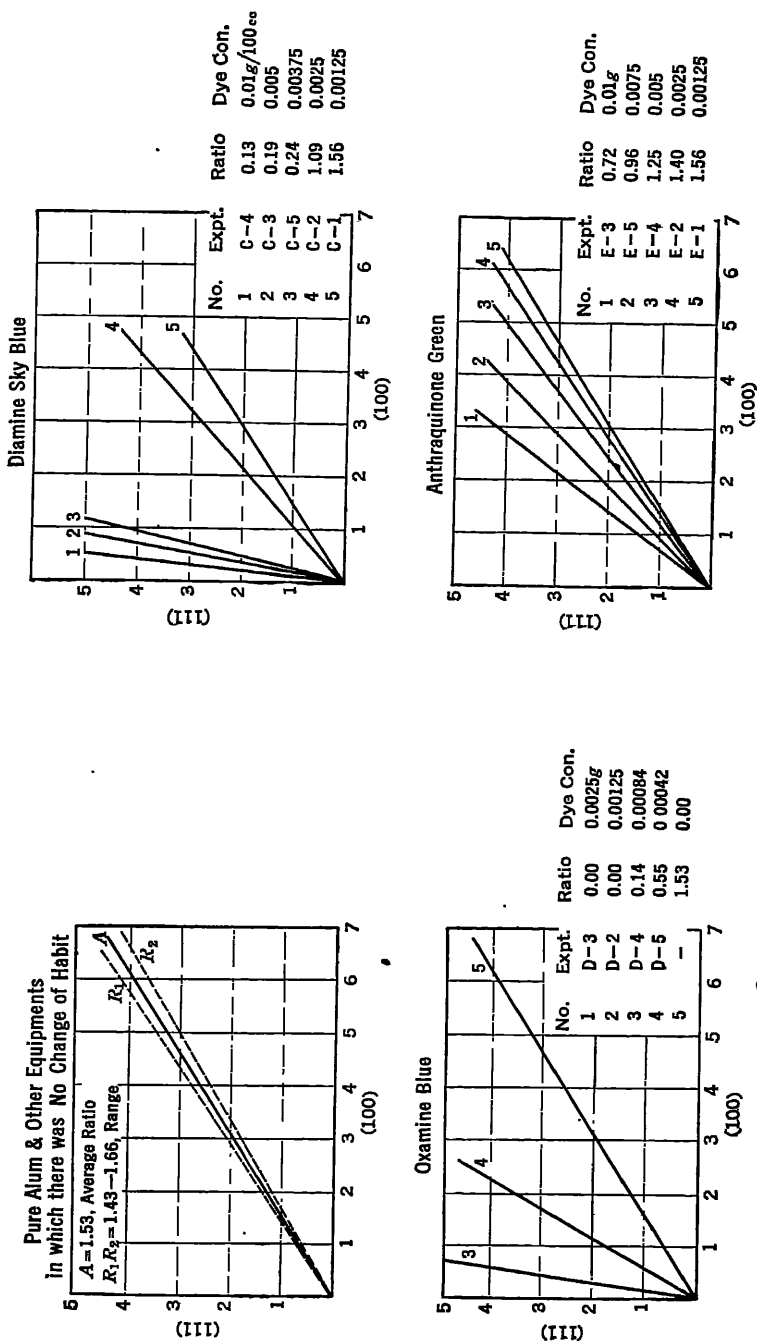
contains a list of the foreign substances added to the alum solution. Table 3 is a summary of the growth ratios measured. The procedure

TABLE 3—SUMMARY OF AMMONIUM ALUM GROWTH RATIOS

Dye Added to Solution	Concentration (Gm. per 100 cc.)	Ratio	Deviation (Per Cent)
Pure alum solution.....		1.51	-1.3
Pure alum solution.....		1.55	+1.3
Pure alum solution.....		1.43	-7.0
Pure alum solution.....		1.55	+1.3
Pure alum solution.....		1.56	+1.9
Bismarck brown.....	0.005	1.50	-1.9
Bismarck brown.....	0.005	1.58	+3.1
Bismarck brown.....	0.01	1.64	+7.2
Asparagine.....	0.5	1.50	-1.9
Phenylaminoacetic acid.....	0.2	1.50	-1.9
Gelatin.....	0.125	1.66	+7.9
Gelatin.....	0.25	1.46	-4.9
Gelatin.....	0.5	1.54	+0.7
Crystal violet.....	0.0006	1.52	-0.7
Crystal violet.....	0.0025	1.46	-4.9
Formalin.....	1 cc.	1.48	-3.1
No dye.....	General average	1.53	±3.2
Diamine sky blue FF.....	0.00125	1.56	
Diamine sky blue FF.....	0.0025	1.10	
Diamine sky blue FF.....	0.00375	0.24	
Diamine sky blue FF.....	0.005	0.19	
Diamine sky blue FF.....	0.01	0.13	
Oxamine blue B.....	0.00042	0.55	
Oxamine blue B.....	0.00084	0.15	
Oxamine blue B.....	0.005	0.00	
Oxamine blue B.....	0.01	0.00	
Anathraquinone green.....	0.00125	1.56	
Anathraquinone green.....	0.0025	1.40	
Anathraquinone green.....	0.005	1.25	
Anathraquinone green.....	0.0075	0.96	
Anathraquinone green.....	0.01	0.73	

followed for the determination of the growth ratios was the same as for the potassium alum with the following exception. Instead of adding the individual displacements for each growth interval and using the mean of the values in calculating the growth ratio, the following scheme was adopted. The numerical values for the distances between the cube faces were plotted on coordinate paper for each growth interval against the corresponding values for the octahedral faces. The slope of the line drawn between these points then gave the growth ratio sought. These curves are shown in Fig. 4. The greater the slope of these curves the greater is the effect of the dye. The quantitative relation of the





Summary of Growth Ratio Experiments

Fig. 4.—Growth ratios for ammonium alum.

three dyes which were effective in reducing the growth ratio is shown by the curves in Fig. 5. It is interesting to note that out of twenty-one substances soluble in the alum solution only three changed the growth ratio and modified the crystal habit. Attention is also called to the fact that while diamine sky blue is again effective oxamine blue is much more so and further that whereas bismarck brown was active in the case of potassium alum it is without effect on the ammonium alum. These facts again point strongly to the influence of the crystal structure, since the adsorption took place exclusively at those faces having the stronger fields of force. The specific character of the adsorbed material is also indicated.

Gaubert<sup>20</sup> distinguished two distinct and fundamentally different types of coloration of crystals. The first type is accompanied by pro-

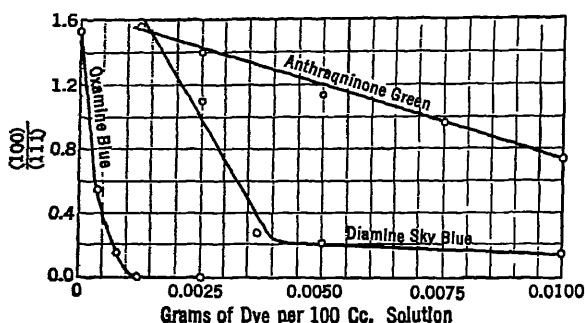


FIG. 5.—Growth ratio-concentration curves for ammonium alum.

found changes in the physical properties of the crystals. The second type produces no such remarkable changes although the crystals are uniformly and distinctly colored. The effect of crystal violet on the ammonium alum belongs to the latter type and the effect of the other dyes belongs to the former.

The selective adsorption of dyes by certain crystal faces gives rise to "hour-glass" patterns reported by Scherr-Thoss,<sup>21</sup> Lehman,<sup>22</sup> Maschke and Vater,<sup>23</sup> and Pellikan.<sup>24</sup> In the case of alum crystals grown on flat surfaces such as the bottom of a dish one would expect as the result of the selective adsorption by the cube planes to have developed a double "hour-glass" pattern having the appearance of a maltese

<sup>20</sup> Compt. rend., 151, 1134 (1910).

<sup>21</sup> Wied. Ann., 6, 284 (1879).

<sup>22</sup> Z. physik. Chem., 8, 543 (1891).

<sup>23</sup> Z. Krist., 33, 57 (1900).

<sup>24</sup> Tschermak's mineral. petrog. Mitt., 13, 258 (1892).

cross on a white field. Figure 6 is a photographic reproduction of an ammonium alum crystal grown in this way in the presence of diamine sky blue. The realization of the predicted pattern is further evidence in support of the belief that the crystal structure is an important factor in adsorption processes.

It was thought desirable to determine if any change in the  $H^+$  ion concentration resulted from the addition of the dye to the alum solution since such changes might reasonably affect the growth process. The pH values of these solutions were measured with a quinhydrone electrode checked with standard buffer solutions. The results are recorded in Table 4 and show no measurable differences from the pure alum solution.

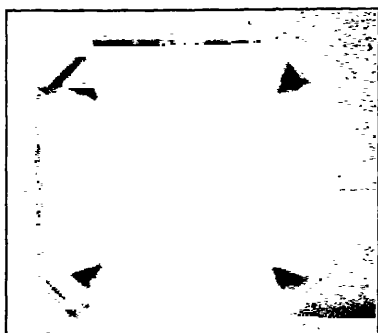


FIG. 6.—Double hour glass pattern, produced by adsorption of diamine sky blue at the (100) faces of an ammonium alum crystal.

TABLE 4—AMMONIUM ALUM pH VALUES

Alum Solution Containing	E. Obs.	pH	Alum Solution Containing	E. Obs.	pH
Pure alum solution....	0.280	2.94	Bismarck brown....	0.280	2.94
Pure alum solution....	0.280	2.94	Asparagine.....	0.283	2.89
Pure alum solution....	0.280	2.94	Phenylaminoacetic		
Anthraquinone green..	0.280	2.94	acid.....	0.280	2.94
Oxamine blue.....	0.280	2.94	Gelatin.....	0.280	2.94
Diamine sky blue.....	0.280	2.94	Formalin.....	0.286	2.82
Crystal violet.....	0.280	2.94			

The dyes both in pure water and in alum solutions were examined with a Zeiss cardioid and with a Zsigmondy slit ultramicroscope to determine their state of dispersion. Some colloid particles were detected in each case, but there appeared to be no relation between the number of particles present and the action of the dye in repressing the face displacement.

Further experiments were made in which a new series of eighteen dyes and thirty-nine simpler organic compounds were used. None of the latter and but four of the dyes were effective in modifying the growth

ratio of ammonium alum. Table 5 contains the complete list of materials added and their effect on the crystal. Only those dyes which were adsorbed appear in this table and they are designated by numbers. Table 6 contains the numbers and structural formulas of the eighteen dyes.

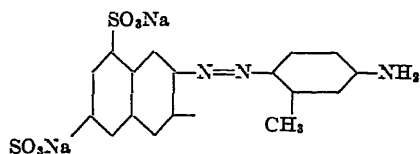
TABLE 5—EFFECT OF FOREIGN SUBSTANCE ON CRYSTAL HABIT OF AMMONIUM ALUM

Compound Added with No Effect on Ammonium Alum Crystal	Compound Added with No Effect on Ammonium Alum Crystal
Acetamide Hydroquinone Hexamethylene tetramine Raffinose Hippuric acid Leucin Alanin Phenylalanin Guanidine chlorhydrate Cocaine hydrochloride Phthalimide Diphenylamine 2,4 Dinitro phenol Propyl resorcinol Benzidine Picric acid Para magnesium phenol sulfonate Beta naphthalene sulfonic acid Para toluene sulfonyl aniline	Sodium-p-toluene sulfonate Sulfanilic acid 2 Amino toluene 4 sulfonic acid Alpha naphthylamine chloride Hydroxylamine hydrochloride Hydrazine hydrochloride Sodium-p-phenol azobenzene sulfonate Ortho aminophenol Acetoxime Ethyl urethane Ethyl-p-toluene sulfonate Benzidine sulfate 2 Naphthylamine 7 sulfonic acid Dicyandiamid Acetaldehyde sodium bisulfite Ethyl chlorohydrin Acetaldehyde Methyl p-amidophenol Glycine
Compound Added	Effect on Ammonium Alum Crystal
No. 4.....	Colorless cube
No. 11.....	Cube, (100) faces light brown
No. 12.....	When used in high concentration (100) faces were approximately equal to (111) faces in size, colored slightly purple.
No. 13.....	Crystals cubic, (100) faces blue

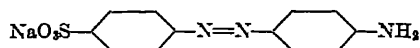
These dyes were of a high degree of purity and it is believed that the effects observed are the result of the action of the dyes rather than of any impurities present. Such impurities as NaCl, alpha-naphthylamine, and diphenylamine which may be present in small amounts were found to

TABLE 6—DYE FORMULAS

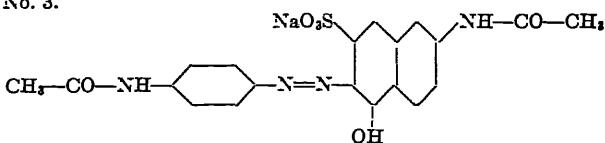
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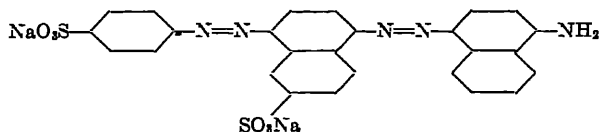
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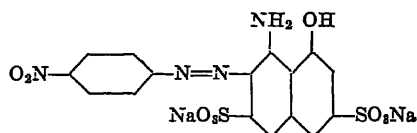
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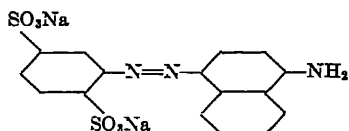
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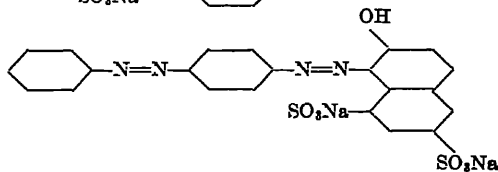
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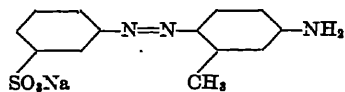
No. 6



No. 7.



No. 8



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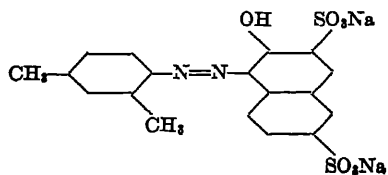
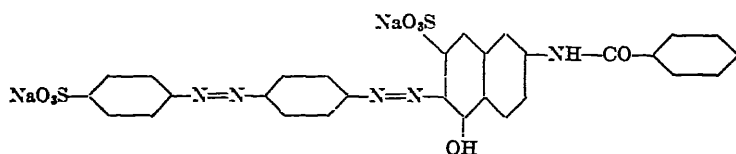
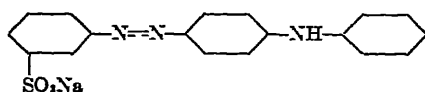


TABLE 6—DYE FORMULAS—*Continued*

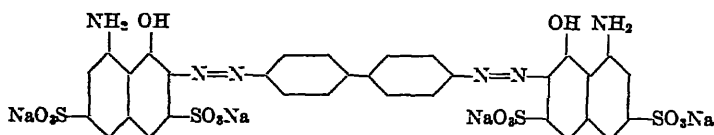
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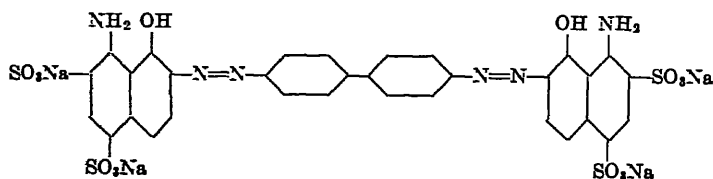
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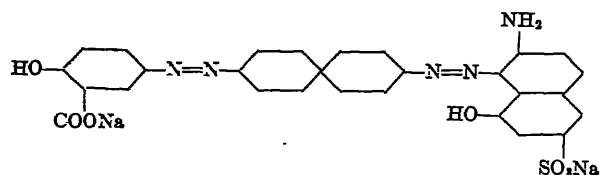
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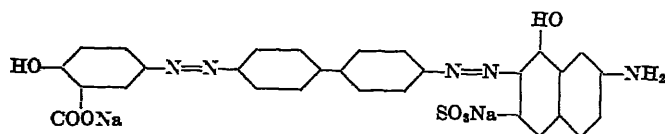
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No. 14.



No. 15.



No. 16.

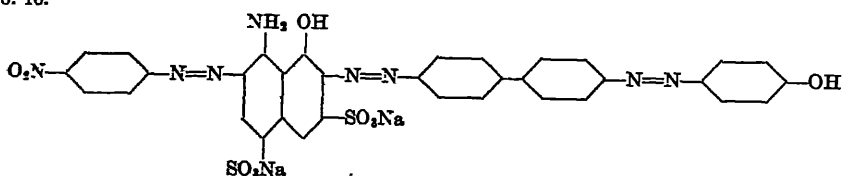
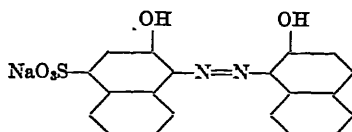
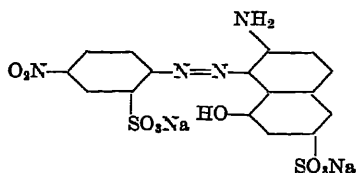


TABLE 6—DYE FORMULAS—*Continued*

No. 17.



No. 18.



be without effect on the alum even when present in concentrations as high as one-half per cent.

The action of these dyes on potassium alum was also determined and the results were the same as for the ammonium alum except for dye No. 12 which was without effect in this case.

It was thought desirable to learn if those dyes which modified the habit of potassium and ammonium alums would produce the same effects on cesium alum. Due to the low solubility of cesium alum only small crystals were obtained and no growth ratios were measured. The dyes were added to the saturated alum solution which was permitted to evaporate slowly. The crystals formed were removed and examined with a microscope.

Dye 13 which modified the habit of both the ammonium and potassium alums colored the crystals uniformly but did not change their shape.

Dye 12 which repressed the perpendicular displacement of the cube faces of ammonium alum to a small extent, and left potassium alum unaffected, had no effect upon the crystal habit of cesium alum, although the crystals were uniformly colored.

Oxamine blue and dye 11, both of which were effective in modifying the growth of ammonium and potassium alum act similarly upon cesium alum.

Bismarck brown, which does not modify the growth of ammonium alum, and which affects the growth ratio of potassium, was found to have a very pronounced effect upon cesium alum. The crystals produced were brown and nearly perfect cubes.

Growth ratio measurements were made using dyes 4 and 13. Dye 12 had no measurable effect upon the growth of ammonium alum unless

used in a very high concentration. At the concentration necessary to affect the growth ratio, the limited amount of light which passed through the solution was not enough to affect the photographic film. Measurement of the growth ratio using dye 11 was also impossible for similar reasons, particularly because the color of the dye in alum solution is deep red which rendered the transmitted light low in actinic value. Figure 7 shows the quantitative effect of these dyes on the growth ratio of ammonium alum.

The dye solutions of the alums were again examined ultramicroscopically and as in the previous cases no relation was found between the colloidal content and the action of the dyes. In connection with these

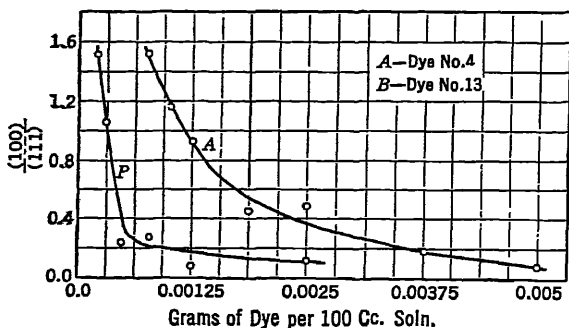


Fig. 7.—Growth ratio-concentration curves for ammonium alum.

observations the sign of the charge of the colloid particles present in the solutions was determined. Of the dyes diamine sky blue, oxamine blue, anthraquinone green, bismarck brown, 4, 5, 11, 12, and 13 all were negative except bismarck brown which was positive.

## II. EQUILIBRIUM IN THE SYSTEM: ALUM CRYSTAL—SATURATED ALUM SOLUTION—DYE

According to Marc<sup>25</sup> the equilibrium between a crystal and its saturated solution containing a dye is not kinetic in character. This conclusion was reached by noting that the solution velocity of crystals colored with dyes was independent of the dye concentration of the solution in which the crystals were dissolved, whereas the growth velocity was greatly retarded by the presence of dyes in the solutions in which the crystals were grown. From these two relations one might expect

<sup>25</sup> Marc: *Z. physik. Chem.*, **73**, 685 (1910).



interesting results if a crystal which is capable of adsorbing a dye is suspended in a solution of that salt containing such dye, but so arranged that no evaporation takes place. Such an experiment was performed. A bottle of potassium alum solution saturated at  $30^{\circ}\text{C}$ . and containing oxamine blue dye was placed in a water thermostat, the temperature of which was  $30.0^{\circ} \pm 0.1^{\circ}\text{C}$ . The bottle was closed with a cork bearing a platinum wire on the lower end of which was fastened a crystal of potassium alum. The wire was of such length that the crystal was suspended in the central part of the solution.

If the equilibrium in this system were kinetic in character, then one should expect the dye to be adsorbed on the cube faces. Owing to the difference in the solution and growth velocities it is apparent that the cube face should broaden out, for the molecules would be leaving the cube faces faster than they would be coming to these faces. As a matter of fact, after two weeks no such change was detected. Another experiment with potassium alum and diamine sky blue gave similar results.

In this connection the following quantitative determination was made with ammonium alum.

A 250-cc. bottle of ammonium alum solution saturated at  $25^{\circ}\text{C}$ . and containing 0.005 per cent of dye 13, was placed in a water thermostat, the temperature of which was  $25.0^{\circ} \pm 0.1^{\circ}\text{C}$ . The bottle was closed by a paraffined cork bearing a nichrome wire on the lower end of which was fastened a weighed crystal of ammonium alum. The area of its cube faces had been determined with a microscope with an accuracy of  $\pm 0.1\text{ mm}^2$ . After two weeks the crystal was removed, dried, weighed, and the area of its cube faces again measured.

Weight of crystal when placed in solution. . . . 0.8968 gm.

Weight of crystal when removed from solution 0.8773 gm.

This loss in weight (2.2 per cent) may have been due to incomplete saturation of the solution.

Area of cube faces of crystal when placed in solution. . . . .	11.2 mm <sup>2</sup> .
Area of cube faces of crystal when removed from solution. . . . .	10.4 mm <sup>2</sup> .
Decrease in area of cube faces. . . . .	0.8 mm <sup>2</sup> .
	or 7.0 per cent

No detectable quantity of dye was adsorbed on the cube faces. One may conclude, therefore, that the magnitude of the forces responsible for the adsorption of the dyes on the cube faces is different in a solution at equilibrium than it is in a solution which is freely evaporating.

### III. RELATION BETWEEN WEIGHT OF DYE ADSORBED AND AREA OF ADSORBING SURFACE

The shape of the curves in Figs. 3, 5, and 7 suggests the possibility that at small values for the growth ratios, some of the dyes may be adsorbed in monomolecular layers. To accurately determine whether the dye is present as a continuous monomolecular layer in the crystals requires information and a technique not at present available. However, as an interesting bit of speculation and in the absence of something more exact, the following calculation was made. The weight of diamine sky blue adsorbed by the cube faces, of known area, of a number of ammonium alum crystals was determined colorometrically. Using this value, the molecular weight of the dye and the Avogadro constant the number of molecules present was calculated. From the values given for the areas of the naphthalene and benzene groups, by W. H. and W. L. Bragg<sup>26</sup> the total area covered by the two benzene and the two naphthalene groups in the diamine sky blue molecule is found to be  $180 \text{ \AA}^2$ . The attached groups probably do not lie wholly in the same plane and therefore occupy a relatively small area. To allow for this area  $300 \text{ \AA}^2$  was assumed to be the total area covered by a single diamine sky blue molecule. The total area which would be covered by a monomolecular layer of the dye was then calculated by multiplying the value  $300 \text{ \AA}^2$  by the total number of dye molecules adsorbed. Since the perpendicular displacement of the cube faces during growth was known, then from the dimensions of the unit cell and the distribution of the cube planes within the cell the total area of the ionic planes at which adsorption occurred was calculated. If the dye is present as monomolecular layers then the two values for the calculated areas should agree. In this case the area of the cube planes was 4300 times greater than the area that could have been covered by the number of dye molecules adsorbed. From the calculation it seems probable that there is not a monomolecular layer of dye molecules present forming a continuous coating over the ionic planes. It is, of course, realized that this calculation is far from exact and at best can only be regarded as a very rough approximation.

### EFFECT OF DYE ADSORPTION ON INTERFACIAL ANGLES OF AMMONIUM ALUM

A two-circle goniometer was used to measure the angle between the cube and octahedral faces of an ammonium alum crystal grown in the presence of 0.005 per cent dye No. 13. The normal value for this angle is  $54^\circ 44'$ .

<sup>26</sup> "X-Rays and Crystal Structure," Chap. 14, 4th Ed. (1924).

The angles measured were

$$\begin{aligned} 54^{\circ} 42' \\ 54^{\circ} 38' \\ 54^{\circ} 39\frac{1}{2}' \end{aligned}$$

*Lead Nitrate.*—Lead nitrate has been found by Vegard<sup>27</sup> to belong to the tetrahedral-pentagonal dodecahedral class of the cubic system. Its structure is such that the cube planes are populated alternately by lead ions and then by nitrate ions. This same relation also holds for the octahedral planes except that the interionic distances within the planes are not the same in both cases. Under these conditions the fields of force at the cube and octahedral faces would not be of the same intensity even though they are populated by ions of like charge.

In the work on the alums it was found that when a foreign substance was adsorbed the adsorption took place on the faces populated by ions of like charge. It was further found that not all substances were adsorbed at these faces and also that the same substance was not always adsorbed by the different alums. In each case the growth ratio  $V_{100}/V_{111}$  was reduced and the crystal habit was modified. If this effect is general, then from the structure of lead nitrate one might expect that foreign substances would be adsorbed at either the cube or octahedral faces, depending upon the specific properties of the foreign substances. The value  $V_{100}/V_{111}$  would be reduced in the one case with cubes being formed, and increased in the other with octahedra resulting.

The effect of twenty dyes on lead nitrate was investigated in the way already described. Recrystallized lead nitrate crystals were used. They were cubo-octahedral with occasional hemihedral faces of the pentagonal dodecahedra. Two of the dyes were adsorbed, methylene blue and bismarck brown. The former produced perfect cubes, blue in color and the latter perfect octahedra, brown in color. The  $V_{100}/V_{111}$  ratio was reduced to zero with a concentration of 0.00125 gram of methylene blue per 100 cc. of solution. The  $V_{100}/V_{111}$  ratio with bismarck brown was not determined. All of the solutions were examined ultramicroscopically but no differences were found that served to distinguish those solutions in which adsorption had occurred from those in which there was none. These results again indicate the influence of the structure of the crystal on the adsorption process and also the specific action of the dyes.

<sup>27</sup> Z. Physik., 9, 395 (1922).

## IV. DISCUSSION

The adsorption of foreign materials by crystal faces and the modification of crystal habit presents many interesting problems. In attempting to account for such phenomena a number of facts must be considered. The principal ones noted in the present series of experiments are the following: (1) Usually when a crystal adsorbs foreign materials the adsorption is selective for certain faces. An exception to this was found in the case of crystal violet which colored ammonium alum at all faces but did not affect the crystal habit. (2) A given foreign material may be adsorbed by one crystalline substance and not at all by a closely related one. Thus bismarck brown was adsorbed by potassium alum and cesium alum but not by ammonium alum. (3) In the cases in which dyes were adsorbed only those faces populated by ions of like charge were colored and had their perpendicular displacements repressed. The direction of change in the growth ratios was in agreement with this effect. (4) The quantitative effect of the foreign material in modifying the habit of a given crystal varies with the adsorbed material. This is illustrated in the case of ammonium alum where a concentration of 0.00125 gm. oxamine blue and anthraquinone green per 100 cc. reduced this value to 0.13 and 0.73, respectively. (5) The pH values of the ammonium alum solutions were not changed by the presence of the foreign materials which were adsorbed. (6) The ultramicroscopic examinations revealed no characteristic differences existing between those solutions from which adsorption had occurred and those from which there was none. (7) The interfacial angles of ammonium alum are unchanged by the adsorption of dye. (8) Chemically similar foreign materials do not produce quantitatively the same results with the same crystalline substance. Thus in the case dyes 12 and 13, which are isomeric, the former is measurably adsorbed by ammonium alum only at very high concentrations, whereas the latter is readily adsorbed at very low concentrations. (9) No measurable adsorption occurs unless the crystal is actually growing in the presence of the foreign material. (10) Polar groups were present in each of the foreign materials which were adsorbed.

Niggli<sup>28</sup> has advanced an illuminating theory of the growth of crystals. Beginning with the space lattice of the sodium chloride type, he pictured the residual valences as having components in the six directions of a cube. It is shown that planes passing through such a lattice vary in density of population by ions, and that just below the plane which comprises the crystal face, there is a layer of ions whose residual

<sup>28</sup> Z. anorg. Chem., 110, 55 (1920).

valences are not all brought into play. The velocity of perpendicular displacement of a face is proportional to the thickness of such a layer, which is maximum for the vicinal faces and zero for the more prominent faces.

According to Niggli's theory, in the case of crystals growing in the presence of foreign substances it is probable that only those ions actually in the crystal face are responsible for the adsorption of the foreign substance. The unused valences in the crystallographically unsatisfied layer beneath the crystal face are probably used almost entirely to cause perpendicular face displacement. The evidence for this is that the adsorption of the foreign materials never takes place on vicinal faces. In a face populated by one kind of ion there is a strong adsorptive effect provided the thickness of the unsatisfied layer is zero, whereas in a face populated equally by oppositely charged ions, there is a partial polarization of the residual valences where these overlap. If crystal growth were due to the whole of the residual valence forces, one should expect the (110) and the (111) faces to grow outward most rapidly, whereas, they are the slower growing faces. Vicinal faces have the greater velocity of perpendicular displacement.

In general the growth forces appear to be greater than the adsorptive forces, hence vicinal faces disappear as the crystal grows, and for this reason adsorption takes place only on the prominent faces. Adsorption occurs at faces populated by like ions because here the forces are stronger than on the faces of the "checker-board" type where the residual valences are partially polarized. While these hypotheses explain many of the growth phenomena of crystals, they do not adequately account for the widely different results obtained in the adsorption of various substances at crystal-solution interfaces. It seems necessary, therefore, in order to account for the results obtained in this work to extend the hypotheses so as to include considerations of the size of the ions and the interionic distances in the crystal lattice; the nature of the residual force fields in the polar groups of the adsorbed material and also their spatial arrangement within the adsorbed molecule or ion.

Adsorption is apparently closely related to crystal growth in the cases studied. Thus in the experiments previously described, the alum crystals adsorbed no measurable quantity of dye when suspended in saturated alum solutions containing dyes, the experiment being so arranged that no evaporation took place. From this it would seem that the forces causing adsorption on a crystal face during growth are absent or reduced to such an extent as to be ineffective at equilibrium.

Apparently the facts enumerated in items (1) and (3) above can be accounted for on the basis of the structure of the crystal. When the

structure is such that the ions or atoms comprising the crystal are so arranged that certain planes have stronger fields of force than others, then it is reasonable to expect adsorption to occur at the planes of stronger force. Many of the foreign materials which were not adsorbed also contained polar groups, therefore in considering item (10) it would appear that the distribution of these groups within the molecule may be a factor. The quantitative effect is perhaps determined on the one hand by the interionic distances within the crystal and the magnitude of the force fields at the crystal face, and on the other hand by the size and shape of the adsorbed molecule or ion, the distribution of polar groups within it and by the magnitude of its residual valency forces. With these ideas in mind the following explanation is tentatively offered. During growth one may imagine that the whole crystal face is not ionically plane, but that all over the face columns of ions are building up. This concept is not in conflict with the law of parallel face displacement, for each column may be considered as a crystal in itself. The solution pressures of such points would probably be such that they could not grow large enough to prevent the displacement of the faces as a whole. The distance between two such ionic columns would depend on the interionic distances in the lattice. If now the distances between two such columns and the distance between polar groups in the adsorbed material were just right, adsorption of the foreign material across two of these columns could take place. Under these conditions when the crystal face is covered with a monomolecular layer of dye, the thickness of such a layer in all probability would not be the thickness of the dye molecule, for other ionic columns could grow up between the adsorbed molecules to be capped in turn by adsorption of more dye molecules.

This explanation is in harmony with the results obtained in the determination of the quantity of dye adsorbed per unit of surface in which the total area of the adsorbing surface (if one considers each successive plane of ions a new surface), was found to be very roughly four thousand times the area the dye molecules were capable of covering as a monomolecular layer, assuming that the area covered by a single molecule was  $300 \text{ \AA}^2$ . If this be true, it is apparent that a monomolecular layer in the usual sense does not exist in this adsorption process. The dye molecules adsorbed on the "atomic or ionic columns" probably produce fields of force around these points due to the unsaturation of the polar groups. These force fields may inhibit growth over the entire range of their forces which would extend laterally over considerable area and vertically through several layers or planes of ions.

The break points in the curves in which the growth ratios were plotted against dye concentration may be thought of as representing

not a monomolecular layer of adsorbed dye but a "saturated surface" in which the dye molecules exert an almost completely inhibitory influence upon the further perpendicular displacement of the faces.

The results of this investigation warrant the conclusion that one may be able to predict that if any given crystalline substance is going to adsorb a foreign substance the adsorption will take place at those faces having the strongest fields of force. However, in order to be able to predict just what foreign substances will be adsorbed by the crystal faces, it would appear that more information concerning the size, shape, structure and magnitude of the force fields of the molecules of the foreign materials must be obtained.

The conclusions drawn from this work are not in agreement with those of Saylor<sup>29</sup> who studied the modification of crystal habit by foreign substances. Drops of saturated solutions containing foreign substances were permitted to evaporate at room temperature on microscope half-slides. The development of the crystals was observed through a microscope on the stage of which the half-slides were placed. The following quotation<sup>30</sup> is a statement illustrating his views:

"Using acid and alkaline solutions, their influence upon external crystal form has served as a key to the entire field of adsorption and has tied in with those examples where adsorption can actually be demonstrated. This new technique is absolutely general; it applies to all crystal systems; it applies to crystals growing from solvents other than water; and it can be applied to crystals growing from a melt if the chemistry of the melt is understood sufficiently."

From this the conclusion is drawn that if a given habit results from growth in an acid medium it is due to the adsorption of hydrogen ions and therefore all readily adsorbed cations will produce the same form. If another habit is favored when the crystal is grown in an alkaline medium, this is due to the adsorption of hydroxyl ions and therefore all readily adsorbed anions will produce this form. The statement is also made (p. 1445) that "Negative ions are adsorbed on the octahedron faces of the alkali halides and barium nitrate, on the cube faces of potassium alum, and on the pyramids of sodium nitrate. The other principal faces adsorb positive ions."

The results obtained in this laboratory certainly are not in harmony with the above stated generalization. In all the cases studied in which adsorption and modification of the crystal habit occurred the growth ratio varied in such a way as to indicate adsorption only by those faces

<sup>29</sup> Saylor: Bancroft's "Applied Colloid Chemistry," 2nd Ed., 198 (1926); Colloid Symposium Monograph, 5, 49 (1928); J. Phys. Chem., 32, 1441 (1928).

<sup>30</sup> Saylor: J. Phys. Chem., 32, 1446 (1928).

populated by ions of like charge. If the other principal faces adsorbed any material at all the effect on the repression of the perpendicular displacement of such faces was negligible in comparison to the effect on the other faces.

In an attempt to reconcile the results reported in an earlier paper<sup>31</sup> on potassium alum and dyes with his generalization, Saylor decides on the basis of some diffusion experiments that diamine sky blue and bismarck brown are not in true solution, but that naphthol yellow, quinoline yellow, methyl violet and methylene blue are. He states: "The dyes which are in true solution do not alter the crystal form of potassium alum." Since the diffusion velocities reported by him seemed excessively high (20 cm. in two days at room temperature for potassium permanganate, methyl violet, naphthol yellow and methylene blue), they were redetermined. The maximum diffusion in five weeks time was but 15 cm. The diffusion constants for naphthol yellow, methylene blue, quinoline yellow, diamine sky blue and bismarck brown were found to be 19, 22, 12, 4 and 8, respectively. The use of these diffusion velocities as a criterion for molecular dispersion would lead to the conclusion that both naphthol yellow and bismarck brown are similarly dispersed. Diamine sky blue has a molecular weight about three times that of either naphthol yellow or bismarck brown. Its diffusion velocity would therefore be expected to be appreciably less than that of the other two dyes.

If Saylor's generalization is correct then one would expect that all basic dyes forming readily adsorbed cations would produce the same habit in the same crystalline substance. This is not the case when lead nitrate is grown in the presence of bismarck brown and methylene blue. Both of these basic dyes are adsorbed but the former produces octahedra and the latter cubes.

From these considerations it seems that no simple rule has yet been found that enables one to predict just what foreign materials will be adsorbed by any one crystalline substance.

### CONCLUSIONS

1. The results obtained in these investigations have been found to be in harmony with the theory that adsorption by a growing crystal is dependent on (1) the residual valency force fields of the crystal faces; (2) the interionic distances within the faces; and (3) the presence and distribution of polar groups in the adsorbed material.

2. The study of the state of dispersion of dyes in alum and lead nitrate solutions indicates that adsorption does not depend upon the dye

<sup>31</sup> Keenen and France: *loc. cit.*



being present in the colloidal state, although colloidal material may be adsorbed.

3. The quantity of dye adsorbed by a growing crystal is believed to be dependent upon its concentration in the solution and upon the area of the adsorbing surface.

4. On the basis of the determination of growth ratios, and the weight of adsorbed dye together with the area of the adsorbing surface, it may be reasonably concluded that there is a minimum concentration of dye in the solution at which the dye is adsorbed to form a "saturated surface"; and that the dye may be present on this "saturated surface" in an amount many times less than that required for a continuous monomolecular layer.

5. Adsorption of the foreign materials used in this work, by growing crystals of ammonium, cesium and potassium alums and lead nitrate, occurs at those faces having the stronger electrical force fields.

6. There appears to be no simple rule whereby one can predict what foreign materials will be adsorbed by any given crystalline substance.

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# SIGNIFICANCE OF THE ELECTROCAPILLARY CURVE

BY A. FRUMKIN

APPLYING Gibbs'<sup>1</sup> theory of surface equilibria to the interface mercury-solution it is easy to show<sup>2</sup> that the following relation must hold:

$$d\sigma = Ed\phi - \sum \Gamma_i d\mu_i \quad (1)$$

In equation (1),  $\sigma$  is the interfacial tension,  $\phi$  the potential difference between solution and mercury, and  $E$  the charge carried by the amount of mercury ions which must be introduced in the solution in order to keep  $\phi$  constant when the mercury-solution interface is increased by 1 sq. cm. The quantities  $\Gamma_i$  and  $\mu_i$  are the surface densities and thermodynamic potentials of the different independent components of the solution, with the exception of the mercury ion, as the term  $Ed\phi$  is substituted in equation (1) for the term  $-\Gamma_{\text{Hg}_2} d\mu_{\text{Hg}_2}$ . There is no term in (1) relating to water as we fix the position of the interface assuming that the surface density of water  $\Gamma_{\text{H}_2\text{O}}$  is equal to zero. If we change  $\phi$  (*i.e.*, the concentration of mercury ions, which is supposed to be low) polarizing a mercury meniscus in a capillary tube, but keep the concentrations of the other components constant, equation (1) reduces to the well-known Lippmann-Helmholtz equation of the electrocapillary curve

$$\frac{\partial \sigma}{\partial \phi} = E \quad (2)$$

This relation could be tested by different methods<sup>3</sup> and the experimental results have been found to be in satisfactory agreement with the theory.

The value of  $\phi$  which makes  $\frac{\partial \sigma}{\partial \phi}$  and  $E$  equal to zero presents a special interest. We shall denote this value by  $\phi_{\text{max}}$ . The numerical values of  $\phi_{\text{max}}$  (and in general all  $\phi$  values) given in this paper are referred to a

<sup>1</sup> "The Collected Works of J. W. Gibbs," Longmans, Green and Co., 1, 230 (1928).

<sup>2</sup> Frumkin: *Ergebnisse der exakten Naturwissenschaften*, 7, 239-241 (1928).

<sup>3</sup> Frumkin: *Z. physik. Chem.*, 103, 55 (1922); Schofield: *Phil. Mag.*, 50, 641 (1926).

normal calomel electrode. A zero value of  $E$  means that on formation of a fresh mercury surface neither do mercury ions disappear from the solution, nor are they sent into the solution; at this particular point the mercury surface carries therefore no charge. Making this statement, we really use the word "charge" as an abbreviation for "charge acquired by the metal surface through a process of exchange of ions between the metal and the solution." The relation between the change of the concentration of mercury in the solution and the charge of the mercury surface was stated for the first time by Nernst<sup>4</sup>. Krueger<sup>5</sup> suggested that although  $E$  is equal to zero at the point  $\phi = \phi_{\max}$ , the mercury surface can still be negatively charged, the mercury adsorbing an amount of mercury salt, equivalent to the amount of mercury ions which have been sent into the solution by the mercury. It could be shown,<sup>6</sup> however, that the concentration of mercury in the solution at the maximum point is far too small to account for such an adsorption; the assumption of a zero charge of the mercury surface at the maximum of the electrocapillary curve seems therefore to be completely justified. Determinations of electrocapillary curves have been carried out for various solutions by different investigators,<sup>7</sup> and especially by Gouy.<sup>8</sup> They show that the value of  $\phi_{\max}$  changes strongly with the composition of the solution. This means that the potential difference between the solution and the mercury does not vanish when the mercury surface is not charged, at least not in all cases. Gouy has shown<sup>9</sup> that these effects can be explained on the basis of adsorption of ions and molecules present in the solution. This theory has been developed by the present author. It is the aim of this paper to give a brief review of what we can learn about adsorption and orientation of ions and molecules from determinations of  $\phi_{\max}$ .

## I. INORGANIC ELECTROLYTES

The position of the maximum of the electrocapillary curve in solutions of inorganic salts is determined by the nature of the anion. The

<sup>4</sup> Beil: Wied. Ann., 58 (1896); Z. Elektrochem., 4, 29 (1897).

<sup>5</sup> Nachr. Ges. Wiss. Göttingen, Math. physik. Kl., 33 (1904); Krüger and Krumreich: Z. Elektrochem., 19, 617 (1913).

<sup>6</sup> Frumkin: *loc. cit.*, 3, 64.

<sup>7</sup> Paschen. Wied. Ann., 41, 42, 177 (1890); 43, 568 (1891); Smith: Phil. Trans. Roy. Soc., 193, 47 (1900); Rothmund: Z. physik. Chem., 15, 1 (1894); Meyer: Wied. Ann., 45, 508 (1892); 53, 845 (1894); 56, 680 (1895); 67, 733 (1899); Z. physik. Chem., 70, 315 (1910).

<sup>8</sup> Ann. chim. phys., (7) 29, 145 (1903); (8) 8, 291 (1906); (8) 9, 75 (1906).

<sup>9</sup> Ann. phys., (9) 7, 129 (1917).

cation does not exert a marked influence except in the case of small differences which are observed between the curves of some acids and their salts. The character of the influence of the anion can be illustrated in a convenient way by Fig. 1, which is taken from Gouy. There is a large group of salts which raise the maximum value of the interfacial tension  $\sigma_{\max}$  above the value observed in pure water, or at least do not cause a marked lowering of  $\sigma_{\max}$ . Carbonates, phosphates, arsenates, sulphates and hydroxides belong to this group. The values of  $\phi_{\max}$  which are observed in normal solutions of these salts lie between the limits 0.47 and 0.52 volt. Salts of other anions lower  $\sigma_{\max}$  more or less and cause a shift of the maximum toward increasing values of  $\phi$ , as is shown in Fig. 1. The following values of  $\phi_{\max}$

are observed in normal solutions of some salts:  $\text{NaClO}_4$  0.55,  $\text{KCl}$  0.56,  $\text{KNO}_3$  0.56,  $\text{KBr}$  0.65,  $\text{KCNS}$  0.72,  $\text{KI}$  0.82,  $\text{K}_2\text{S}$  0.92. The depression of the maximum shows that in these solutions there is a positive adsorption of the salt on an uncharged surface of mercury. The fact that as a result of this adsorption the maximum is shifted toward increasing values of  $\phi$  can be explained if we assume that the adsorbed salt forms a double layer at the mercury-water interface, its anions being turned toward the mercury phase. This theory which was proposed by Gouy accounts also for the difference in the rôle of the

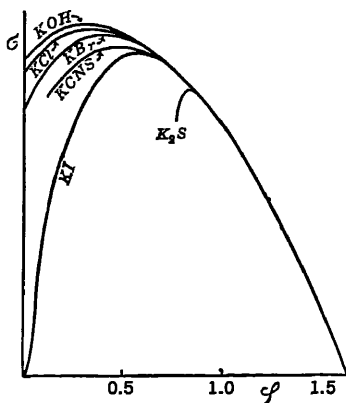
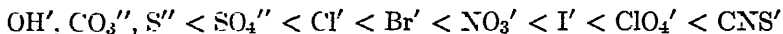


FIG. 1.—Electrocapillary curves of solutions of different inorganic electrolytes.

cation and the anion, as the anions are held in this double layer by specific adsorptive forces, whereas the cations are electrostatically attracted by the negative charges of the anions. It is interesting to compare the order of adsorbability of anions at the mercury-water interface which can be determined in this way from electrocapillary measurements with the order of adsorbability at the water-air interface. The author, using an electrostatic method showed<sup>10</sup> that the surface of many salt solutions are negatively charged at higher concentrations compared to pure water, indicating the presence of an excess of anions in the outer part of the surface layer. The results of these electrostatic measurements were corroborated by measurements of surface tension. The

<sup>10</sup> Z. physik. Chem., 109, 34 (1924); Frumkin, Reichstein and Kulvarskaja: Kolloid-Z., 40, 9 (1926).

following order of increasing adsorbability of anions at the air-water interface was established:



It is probable that this is also the order of decreasing energies of hydration of the ions, at least for ions of a similar structure. If we compare the behavior of anions at the two interfaces water-air and water-mercury we see that for many ions the order of increasing adsorbability is the same in both cases. With other ions, however, there is a pronounced specific influence of the mercury surface. The most striking example is given by the  $\text{S}''$  anion which is at the beginning of the series in the case of the air-water interface and at the end of the series in the case of the mercury-water interface. The adsorbabilities of the halogen ions compared to the  $\text{NO}_3'$  and  $\text{ClO}_4'$  ions are also much greater in contact with mercury.

## II. ORGANIC COMPOUNDS

Solutions of organic non-electrolytes have been extensively investigated by Gouy<sup>11</sup> and some additional measurements have been carried

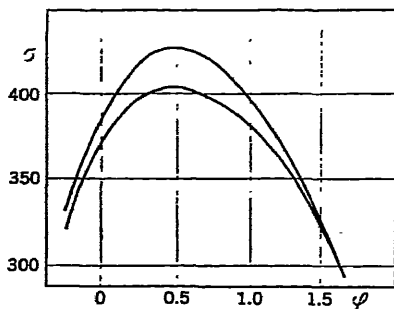


FIG. 2.— $n\text{Na}_2\text{SO}_4$  and  $n\text{Na}_2\text{SO}_4 + \text{Saccharose}$ .

out by the author in collaboration with Donde and Kulvaskaja. It is convenient to compare the electrocapillary curve, which is observed after the addition of the organic substance, with the original curve of the solution which contains the inorganic electrolyte only. This is shown in Figs. 2, 3, and 4. So far as the position of the maximum is involved, the organic substances can be divided into three classes: (1) those which do not materially change the value of  $\phi_{\text{max}}$  (Fig. 2); (2) those which shift the maximum to smaller values of  $\phi$  (Fig. 3); (3) those which shift it to larger values of  $\phi$  (Fig. 4). The shape of the curves which is observed in solutions of organic substances is sometimes quite characteristic, as is shown by Fig. 3. This indicates that the adsorption of the organic molecule varies strongly with the surface charge of the mercury. A mathematical treatment of this problem has been given by the author,<sup>12</sup>

<sup>11</sup> Ann. chim. phys., (7) 29, 145 (1903); (8) 8, 291 (1906); (8) 9, 75 (1906).

<sup>12</sup> Z. Physik., 35, 792 (1926); Frumkin and Obrutschewa: Biochem. Z., 182, 220 (1927); Obrutschewa: *Ibid.*, 207, 25 (1929).

but it will not be discussed in this paper. The observed shift of the maximum shows that the existence of an adsorbed layer of molecules of substances belonging to groups 2 and 3 produces a potential difference between the mercury and the solution. This was pointed out for the first time by Gouy. If we disregard the effect caused by the water molecules themselves, this potential difference is positive for group 2 (positive end of the molecule turned toward the mercury), and negative for group 3 (negative end of the molecule turned toward the mercury). It was shown by the experiments of Kenrick,<sup>13</sup> Guyot,<sup>14</sup>

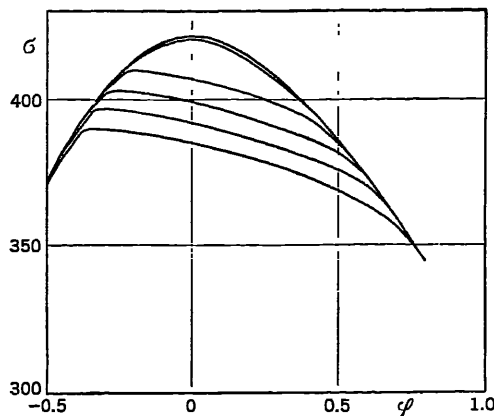


FIG. 3.— $n\text{NaCl} + x\text{C}_8\text{H}_{17}\text{OH}$ ,  $x = 0, \frac{1}{100}, \frac{1}{50}, \frac{1}{20}, \frac{1}{10}$  mols per liter.

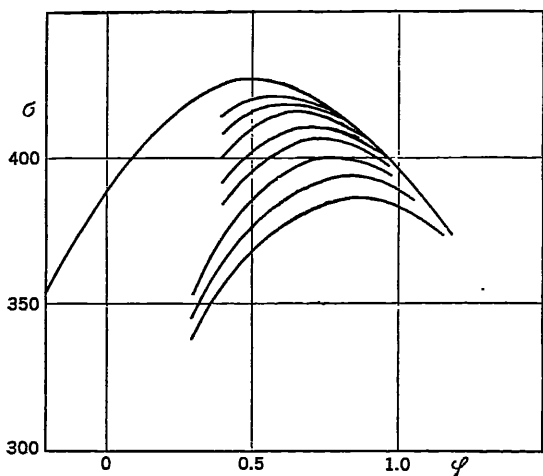


FIG. 4.— $n\text{H}_2\text{SO}_4 + x\text{CS}(\text{NH}_2)_2$ ,  $x = 0, \frac{1}{25}, \frac{1}{10}, \frac{1}{5}, \frac{1}{2}$  mols per liter.

and by those of the author<sup>15</sup> that the adsorption of organic compounds at the air-water interface gives rise to similar electric effects and it seemed worth while to compare the results obtained in both cases. A computation of the available data carried out by the author<sup>16</sup> some time ago is reproduced in Table 1.  $\Delta$  is the lowering of the surface tension of water by the dis-

<sup>13</sup> Z. physik. Chem., 19, 625 (1896).

<sup>14</sup> Ann. phys., (10) 2, 501 (1927).

<sup>15</sup> Z. physik. Chem., 111, 190 (1924); 116, 485 (1925); 123, 321 (1926); Cf. also, Frumkin and Williams: Proc. Nat. Acad. Sci., 15, 400 (1929).

<sup>16</sup> Loc. cit., 2, 258-264; a few misprints which occur in this paper have been corrected here. Cf. also, Harkins and Ewing: J. Am. Chem. Soc., 42, 2539 (1920).

solved substances and  $\epsilon$  is the potential difference at the air-solution interface, assuming a zero value for the potential difference between air and pure water.  $\Delta_{\text{Hg}}$  and  $\epsilon_{\text{Hg}}$  represent the corresponding quantities for the mercury-water interface, *i.e.*,  $\Delta_{\text{Hg}}$  is the lowering of the maximum interfacial tension, caused by the organic substance and  $\epsilon_{\text{Hg}}$  the difference between the value of  $\phi_{\text{max}}$  in a solution of an inactive electrolyte ( $\text{Na}_2\text{SO}_4$ ) and in a solution which contains the organic substance. The latter is identical with the drop of potential connected with the layer of organic molecules adsorbed at the mercury-water interface, if we ascribe a zero value to the potential difference mercury—pure water at the electrocapillary maximum. The values  $\Delta_{\text{Hg}}$  and  $\epsilon_{\text{Hg}}$  refer to solutions which contain some electrolyte, as otherwise the determination of  $\phi_{\text{max}}$  would be impossible. If it is not stated to the contrary this electrolyte is normal  $\text{Na}_2\text{SO}_4$ . As the presence of the electrolyte influences the activity of the dissolved organic substance, the comparison between the values of  $\Delta$  and  $\epsilon$  and the values of  $\Delta_{\text{Hg}}$  and  $\epsilon_{\text{Hg}}$  can be only semi-quantitative. The numerical values given in Table 1 have been taken from different sources. A list of references is given below.<sup>16</sup>

TABLE 1

Substance	Concentration	$\Delta$	$\Delta_{\text{Hg}}$	$\epsilon$	$\epsilon_{\text{Hg}}$
Methyl alcohol.....	molar	7.2	3.3	0.10	0.02
Ethyl alcohol.....	molar	15.9	9.5	0.23	0.08
Propyl alcohol.....	molar	29.1	31.0	0.32	0.24
Iso-amyl alcohol.....	0.1 molar	30.0	31.0	0.25	*~0.25
Tertiary amyl alcohol.....	0.1 molar	20.4	22.6	0.29	0.35
Allyl alcohol.....	molar	21.5	24.2	0.26	0.15
Acetic acid.....	2 molar	17.3	12.2	0.22	0.00
Propionic acid.....	molar	25.0	23.3	0.27	0.11
Normal butyric acid.....	saturated	.....	.....	~0.35	0.14
Normal caproic acid.....	0.07 molar	39.0	36.8 (+0.3 normal $\text{KNO}_3$ )	0.34	0.21
Ether.....	saturated	~43	29.3	~0.52	$\geq 0.38$
Ethyl acetate.....	saturated	.....	.....	~0.58	$\geq 0.43$
Acetone.....	molar	17.4	15.2	0.38	0.25
Paraldehyde.....	saturated	.....	.....	0.36	~0.45
Ammonia.....	molar	2.4	2.4	0.08	0.02
Triethyl amine.....	0.1 molar	22.2	32.3 (without $\text{Na}_2\text{SO}_4$ addition)	0.53	~0.35
Glycol.....	molar	3.1	7.1	0.10	0.03

\* This symbol ( $\sim$ ) means approximate value.



TABLE 1.—Continued

Substance	Concentration	$\Delta$	$\Delta_{Hg}$	$\epsilon$	$\epsilon_{Hg}$
Glycerine.....	molar	0.4	9.3	0.02	0.005
Saccharose.....	molar	-2.0	23.8	0.002	0.00
Oxalic acid.....	0.1 molar	0.3	1.6	-0.004	-0.04
Malonic acid.....	molar	4.2	11.8	-0.006	-0.055
Benzene.....	saturated	$\sim 13$ .	23.1	0.01	0.11
Phenol.....	0.1 molar	11.6	36.6	0.03	-0.15
<i>p</i> -Cresol.....	0.1 molar	20.8	50.0	0.01	-0.20
<i>o</i> -Cresol.....	0.1 molar	28.6	51.5	0.26	-0.29
Anisol.....				0.17	-0.05
				(0.02 molar)	(saturated)
Pyrocatechol.....	0.1 molar	3.0	29.7	-0.01	-0.18
Hydroquinone.....	0.1 molar	1.1	28.0	-0.03	-0.20
Resorcinol.....	0.1 molar	2.1	29.7	-0.04	-0.22
Pyrogallol.....	molar	12.7	40.8	-0.05	-0.25
Aniline.....	0.01 molar	0.3	17.4	0.01	-0.03
Aniline.....	0.1 molar	8.0	46.8	0.12	0.02
<i>o</i> -Toluidine.....	saturated		40.8	0.30	0.05
Nitrobenzene.....	0.007 molar			0.03	-0.25
Benzoic acid.....	0.01 molar	2.0	22.9	0.08	-0.05
<i>o</i> -Phthalic acid.....	0.01 molar			0.02	-0.15
Benzyl alcohol.....	saturated	* $\sim 30.0$	54.9	0.33	0.11
Benzylamine.....	saturated		61.3	$\sim 0.50$	$\sim 0.35$
Chloroform.....	saturated	$\sim 19.0$	20.8	$\sim -0.05$	-0.2
Chloral hydrate.....	molar			-0.37	$\sim -0.35$
Chloracetic acid.....	molar	12.2	24.6	-0.10	-0.09
Trichloroacetic acid.....	molar	22.6	33.6	-0.42	$\sim -0.25$
Bromoacetic acid.....	molar	12.6	38.9	-0.09	$\sim -0.2$
$\beta$ -Chloropropionic acid.....	0.1 molar		14.1	0.02	-0.02
$\beta$ -Iodopropionic acid.....	0.2 molar		73.1		-0.32
Ethyl iodide.....	saturated		39.7	$\sim 0.0$	-0.35
$\beta$ -Chlorobutyric acid.....	0.25 molar		44.6		0.02
Urea.....	molar	-0.3	7.5	0.001	-0.05
Thiourea.....	molar	-0.1	39.7	-0.03	-0.36
			(+ normal $H_2SO_4$ )		
Thioacetic acid.....	0.35 molar		35.0		-0.32
$\alpha$ -Thiolactic acid.....	0.15 molar		40.5		-0.07
Tetra propylammonium chloride	0.1 molar	3.4	16.4	0.24	0.24
			(without $Na_2SO_4$ addition)		

\* This symbol ( $\sim$ ) means approximate value.

The following conclusions can be drawn from Table 1: Aliphatic oxygen compounds with one polar group (alcohols, acids, ethers, esters, ketones) being adsorbed give rise at both interfaces to positive potential differences between the outer phase and the solution. The adsorption and the electric effect are larger at the air-water interface. The difference is greater for acids than for alcohols and decreases with increasing length of the chain. The compounds which contain a sufficient number of carbon atoms exert a very similar action on the mechanical and electrical properties of both interfaces. This shows that the structure of the surface layer must be the same in the two cases. This conclusion is supported by the calculation of the amount adsorbed in the more concentrated solutions.<sup>15</sup> We must assume therefore that at the mercury-water interface there exists the same orientation which is known to exist at the air-water interface, *i.e.*, the polar group must be turned toward the water and the hydrocarbon chain toward the mercury. The introduction of a higher number of polar groups in the molecule of an organic compound lowers, as it is well known, its adsorbability at the air-water surface. This decrease of the adsorbability is much less pronounced at the mercury-water interface. The difference is especially noticeable in the case of saccharose, which is negatively adsorbed at the air-water interface, and positively adsorbed (strongly) at the mercury-water one. The adsorption of saccharose does not give rise to a positive potential difference between mercury and water. We must conclude, therefore, that the orientation of the molecule, which is to be considered as the cause of the electric effect has, disappeared in that case. It is probable that the saccharose molecules lie flat at the mercury-water interface, the polar group of the molecule having the possibility to approach the mercury surface. The interaction between the polar groups and the metal causes an increase of the work of adsorption which partly counterbalances the influence of the increased affinity toward the solvent, which made the adsorption negative in the case of the air-water interface. The adsorption of dibasic acids at the air-water interface causes a slightly negative potential difference between the air and the water. This negative effect is much more pronounced in the presence of mercury. We shall see that this is a general phenomenon: the presence of mercury favors in many cases that kind of orientation of the adsorbed molecule which gives a negative value of  $\epsilon_{Hg}$ . Thus, different phenols which behave in a rather different way at the air-water interface, the univalent phenols giving positive and the polyvalent negative effects, all give very large negative effects and a much greater lowering of interfacial tension at the mercury-water interface. It can also be shown that the adsorbed molecules are much more closely packed in the latter case. Also, the

presence of mercury strongly reduces the differences in the behavior of isomers which are observed at the air-water interface (*cf.* the data for the two cresols and the three dioxybenzols). It would appear that the occurrence of the negative potential difference is connected with the presence of a polar group in the molecule, as benzene itself gives a positive value of  $\epsilon_{\text{Hg}}$ . Although it is difficult at the present moment to give an adequate picture of the structure of these surface layers, it seems hardly possible to account for the high adsorbability of the polyvalent phenols at the mercury-water interface in any other manner than to assume that the polar groups of the phenol molecule are attached to the mercury surface. A similar behavior is indicated in the case of the adsorption of phenols by charcoal.<sup>17</sup> With aniline the value of  $\epsilon_{\text{Hg}}$  changes from negative to positive when the concentration is increased. The shape of the electrocapillary curve which is observed with aniline solutions also indicates that two different orientations of the aniline molecule at the mercury-water interface are possible, one of them giving a positive, and the other a negative effect.

Benzoic acid, benzyl alcohol and benzylamine are all more strongly adsorbed at the mercury-water interface than at the air-water interface; with benzoic acid as with the phenols, the electric effect is negative in the first case and positive in the second case. The specific influence of the mercury surface manifests itself also when halogenated compounds are adsorbed. Many of these give negative values of  $\epsilon$ , which shows that in the surface layer of their solutions the negatively charged halogen atom is turned outward. The  $\epsilon_{\text{Hg}}$  values of substances belonging to this group are negative too, but the lower of the interfacial tension is very much larger when the adsorption occurs at the water-mercury interface. In the case of iodine compounds an enormous lowering of the interfacial tension is observed. This behavior is in complete agreement with the behavior of the iodine ion. If the length of the hydrocarbon chain is increased, the  $\epsilon_{\text{Hg}}$  (and  $\epsilon$ ) values become positive, showing that the hydrocarbon chain occupies the space available in the surface layer and pushes the halogen atom out.

Sulphur compounds, like iodine compounds, are very strongly adsorbed at the mercury-water interface (compare the behavior of the  $\text{S}''$  ion).<sup>18</sup> The case of thiourea which raises the surface tension of water, but causes a great lowering of the interfacial tension and a large negative electric effect at the mercury-water interface, is especially interesting. The adsorption of thiourea at the surface of mercury appears to be in many respects a process quite similar to the formation

<sup>17</sup> Frumkin: *Rec. trav. chim.*, **48**, 288 (1929).

<sup>18</sup> *Cf.* Frumkin: *Kolloid-Z.*, **47**, 229 (1929).

of a complex compound between the mercury ion and the thiourea in a homogeneous solution.

To summarize, we can say that whereas in some cases the structure of the layer adsorbed at both interfaces is practically the same, in other cases large differences are observed, caused by a specific interaction between the mercury surface and definite constituents of the molecule. A negative charge of the part of the molecule which is turned toward mercury seems to favor the possibility of such an interaction.

### III. NON-AQUEOUS SOLUTIONS

As various dissolved substances affect the value of  $\phi_{\max}$  it is natural to assume that the molecules of the solvent can act in a similar way. It appeared therefore worth while to determine the value of  $\phi_{\max}$  in non-aqueous solutions and to compare the results obtained with those which are observed in aqueous solutions of the same electrolytes.<sup>19</sup> The  $\epsilon_{\text{Hg}}$  values in Table 2 indicate the shift of the maximum caused by the substitution of the non-aqueous solvent for water under those conditions when there is no adsorption of the electrolyte. The calculation of these values involves some assumptions which may make them uncertain by a few centivolts; nevertheless there can be no doubt that the position of the maximum depends on the nature of the solvent. The  $E$  values have been obtained by comparing the potential difference air-organic solvent with the potential difference air-water.<sup>20</sup> The substitution of the alcohols and of acetone for water exerts a similar influence in both cases, just as we should expect from the data given in Table 1.

TABLE 2

	$\epsilon$	$\epsilon_{\text{Hg}}$
Methyl alcohol.....	0.38	0.13
Ethyl alcohol.....	0.38	0.20
Acetone.....	0.57	0.33

Table 2 shows also that in absence of any dissolved capillary active substance the molecules of the solvent itself can give rise to a difference of potential between the solution and the mercury which makes the determination of the so-called absolute zero of potential with the help of electrocapillary methods impossible.

<sup>19</sup> Frumkin: *Z. physik. Chem.*, **103**, 43 (1922); *Loc. cit.*, **2**, 267.

<sup>20</sup> *Z. physik. Chem.*, **111**, 190 (1924); **116**, 485 (1925); **123**, 321 (1926); *Cf. also*, Frumkin and Williams: *Proc. Nat. Acad. Sci.*, **15**, 400 (1929).

## V. ELECTROCAPILLARY CURVES OF AMALGAMS AND OTHER METALS

Electrocapillary curves of dilute amalgams of different metals have been investigated by Rothmund,<sup>21</sup> Gouy,<sup>22</sup> and Christiansen.<sup>23</sup> They found that these curves do not differ markedly from the curve of pure mercury, and on this basis it was often assumed that the position of the point of zero charge is independent of the nature of the metallic phase. But with a more concentrated amalgam of a Bi + Pb + Sn alloy Gouy observed a marked shift of  $\phi_{\max}$  and a similar shift was found by

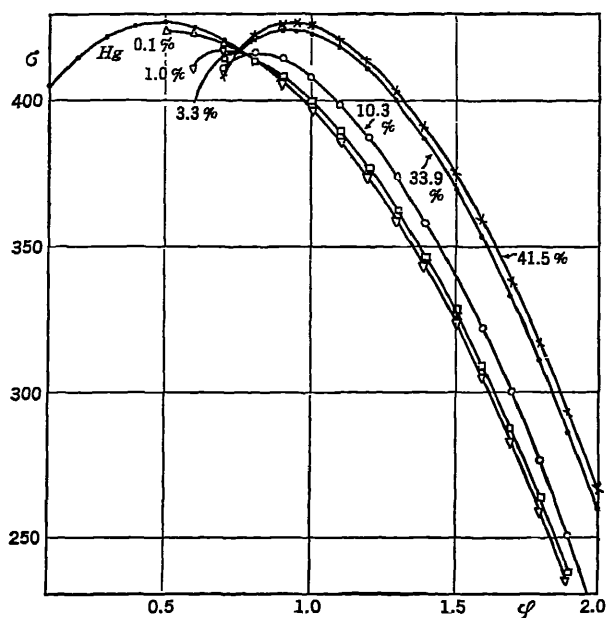


Fig. 5.—Hg and Tl amalgams with 0.1%, 1.0%, 3.3%, 10.3%, 33.9%, and 41.5% Tl in  $n\text{Na}_2\text{SO}_4$ .

Rothmund in the case of a thallium amalgam. Rothmund ascribed it, to be sure, to secondary effects. Frumkin and Gorodetskaya<sup>24</sup> made an extensive study of the behavior of Tl-amalgams in different solutions and found that an addition of thallium causes a large increase of  $\phi_{\max}$  as is shown by Fig. 5 and by the first and second columns of Table 3,

<sup>21</sup> *Loc. cit.*, 7.

<sup>22</sup> *Ann. Phys.*, (9) 6, 5 (1916).

<sup>23</sup> *Drud. Ann.*, 16, 382 (1905).

<sup>24</sup> *Z. physik. Chem.*, 136, 451 (1928).

which gives the values of  $\phi_{\max}$  observed with different amalgams in normal  $\text{Na}_2\text{SO}_4$  solution.

TABLE 3

Per Cent Tl	$\phi_{\max}$	Point of Zero Charge from Dropping Electrode Measurements
0	0.48	
1.0	0.67	0.668
3.35	0.73	
10.35	0.80	0.792
33.9	0.92	0.898
41.5	0.93	

A similar shift was observed with quite different solutions; it cannot therefore depend on a difference in the adsorption of some dissolved substance at the surface of pure mercury and on that of the amalgams. The application of the Gibbs' theory of surface equilibria to the case of a thallium amalgam gives the relation:<sup>25</sup>

$$d\sigma = E dy - \Gamma_{\text{Tl}} d\mu_{\text{Tl}} - \Sigma \Gamma_i d\mu_i \quad (3)$$

The quantity  $E$  has here the same significance as in (1), *i.e.*, it is equal to the electric charge carried by the ions which must be introduced in the solution in order to keep  $\phi$  constant for unit increase of surface. In this equation  $\mu_{\text{Tl}}$  is the thermodynamic potential of the thallium in the amalgam and  $\Gamma_{\text{Tl}}$  is the surface density of thallium or the amount of thallium adsorbed per unit surface, both from the metallic phase and from the solution. The theoretical development shows that an adsorption of the thallium ion cannot be distinguished from the adsorption of thallium dissolved in mercury by experiment. The position of the interface is defined by the condition  $\Gamma_{\text{Hg}} = 0$ . Making certain assumptions it is possible to give by means of equation (3) a complete mathematical treatment of the electrocapillary curves observed with amalgams of different thallium content, but we shall consider here only the simplest case. If the constitution of the amalgam and the solution do not vary, equation (3) reduces as in the case of a pure metal to the Lippman-Helmholtz equation:

$$\frac{\partial \sigma}{\partial \phi} = E$$

<sup>25</sup> Z. physik. Chem., **136**, 451 (1928).

The validity of this equation in the case of amalgams has been tested by F. J. Cirves at the University of Wisconsin.<sup>26</sup> The method used was that of "null solutions," which has been worked out by Palmaer<sup>27</sup> and Smith and Moss.<sup>28</sup> Adding increasing quantities of a thallium salt to a Tl free solution it is possible to find a concentration of Tl ions for which the potential difference between a dropping amalgam electrode and still amalgam is zero. An increase in the amalgam surface at this point causes no change of the concentration of Tl ions in the solution, *i.e.*, the quantity  $E$  is equal to zero. This is the so-called null solution. By determining the e.m.f. of the cell, normal calomel electrode/null solution amalgam, and comparing it with the value of  $\phi_{\max}$  we can test the validity of equation (2). Some of the results obtained by Cirves are summarized in the third column of Table 3. The measurements have been carried out in an hydrogen atmosphere. The agreement between the numbers of the second and third columns must be considered as satisfactory, as the uncertainty in the determination of  $\phi_{\max}$  may amount to 0.01 or even 0.02 volt.

The method of null solutions has been applied by Cirves to Cd-amalgams as well. The position of the point of zero charge of different Cd-amalgams in normal KCl solution and normal KBr solution is given in Table 4. The values for pure mercury have been determined from the corresponding electrocapillary curves.

TABLE 4

Per Cent Cd	Point of Zero Charge	
	Normal KCl	Normal KBr
0	0.56	0.65
0.0003	.....	0.703
0.001	.....	0.711
0.004	0.625	0.724
0.01	0.640	0.736
0.1	0.680	0.760
1.0	0.714	.....
4.8	0.746	0.818

As is shown by Table 4 even a small addition of cadmium to mercury causes a marked shift of  $\phi_{\max}$ .

<sup>26</sup> Unpublished data.

<sup>27</sup> Z. physik. Chem., **59**, 129 (1907).

<sup>28</sup> Phil. Mag., (6) **15**, 478 (1909).

Our information regarding the value of  $\phi_{\max}$  for other metals is rather limited. Hevesy and Lorenz<sup>29</sup> have determined the electrocapillary curves of molten Pb and Sn, but owing to the uncertainty of the reference electrode and differences of temperature it is difficult to compare the position of the maxima. It would appear that the maximum of the Sn and Pb curves are shifted as compared with Hg in the same direction as it is in the case of Tl- and Cd-amalgams. The maximum point of liquid gallium has been determined by Frumkin and Gorodetskaya.<sup>30</sup> The behavior of gallium in alkaline and neutral solutions is complicated by the formation of an oxide film, but in acid solution (normal KCl + 0.1 normal HCl) the value of  $\phi_{\max}$  could be measured with sufficient accuracy and was found to be equal to 0.9 volt. This is practically all we know from direct measurements about the influence of the nature of the metallic phase on the value of  $\phi_{\max}$ . Various methods have been proposed with the purpose of finding the point of zero charge of metallic surfaces, based on other principles. The whole question has been discussed by the present author<sup>31</sup> in another place. It appears to him that the only method whose results can be directly compared with those based on the determination of  $\phi_{\max}$  and on the use of dropping electrodes is the adsorption method which was proposed for the first time by Billitzer.<sup>32</sup> The method is based on the fact that the formation of the double layer at the solid-liquid interface causes definite measurable changes in the composition of the solution if the surface area of the solid substance is large enough. This makes it possible to determine at least the sign of the surface charge. Billitzer tried to apply this method to colloidal platinum and found the point of zero charge at a value of  $\phi$  equal to about  $-0.12$ , but it appears that Billitzer did not take into account one source of error (adsorption of alkali by the products of oxidation of platinum)<sup>33</sup> which makes this value too low. An extensive study of the adsorption of electrolytes by activated charcoal carried out by Bruns and Frumkin<sup>34</sup> led them to the conclusion that activated charcoal acts in this case as a gas electrode and that the zero point for charcoal must lie between the limit  $\phi = 0.2$  and  $\phi = 0.3$ . The zero point for Pt may come into the same interval or even correspond to a still lower value of  $\phi$ , although the value given by Billitzer, as will be shown elsewhere, is certainly too low.

<sup>29</sup> Z. physik. Chem., **74**, 443 (1910).

<sup>30</sup> Z. physik. Chem., **136**, 215 (1928).

<sup>31</sup> Loc. cit., **2**, 271-273.

<sup>32</sup> Z. physik. Chem., **45**, 327 (1903).

<sup>33</sup> Cf. Pennycuik: J. Chem. Soc., **135**, 623 (1929).

<sup>34</sup> Z. physik. Chem. (A) **141**, 141 (1929).



The data which have been obtained for platinum, charcoal, mercury, and the amalgams indicate that the position of the point of zero charge is strongly influenced by the nature of the metallic phase. That means we can build up a cell in which there will be no ionic double layers at the surface of both electrodes and which still will have a definite e.m.f. Thus between mercury and a 41.5 per cent Tl-amalgam, both being polarized in a  $\text{Na}_2\text{SO}_4$  solution so as to make the values of  $E$  equal to zero, there will be a potential difference of 0.45 volt. As there has been no exchange of ions between the metals and the solution in our cell, and no adsorption of ions at the surface of the metals, the potential difference exhibited by the cell may be readily compared to a contact potential difference between metals in a vacuum. It follows therefore from the study of electrocapillary phenomena that contact potentials must constitute an important part of the e.m.f. of ordinary galvanic cells, a result which is certainly contrary to the assumption of the majority of electrochemists. It was found by numerous investigators<sup>35</sup> that the sign of the charge of a metal determined by cataphoretic methods ( $\zeta$ -potential) usually does not agree with the sign which was expected from the position of the metal in the electrochemical series. In many cases this discrepancy must certainly be explained by adsorption phenomena, which complicate the structure of the double layer, as it was shown by Freundlich<sup>36</sup> and Stern,<sup>37</sup> but the theory outlined in this paper indicates still another possibility. As the position of the point of the zero charge changes with the nature of the metallic phase, it appears altogether impossible to find the sign of the charge of a metal from its electrode potential. A metal which would carry a positive charge in a definite solution, if its zero point would coincide with the zero point of mercury, can be in reality negatively charged and vice versa. So long as there are no accurate determinations of the position of the point of zero charge of different metals, we cannot say to what extent the observed discrepancies have to be ascribed to the influence of some adsorption effects on the structure of the double layer. Let us take as an example metallic cadmium. Cataphoretic experiments indicate in some cases a positive charge of the cadmium surface (Coehn and Shafmeister)<sup>35</sup> but it follows from the value of the potential of a cad-

<sup>35</sup> Billitzer: *Z. Elektrochem.*, **8**, 638 (1902); **14**, 624 (1908); **15**, 439 (1909); Garrison: *J. Am. Chem. Soc.*, **45**, 37 (1923); Coehn and Shafmeister: *Z. physik. Chem.*, **125**, 401 (1927).

<sup>36</sup> Freundlich and Rona: *Sitzgsber. preuss. Akad. Wiss. Physik. Math. Kl.*, **20**, 397 (1920); Freundlich and Ettisch: *Z. physik. Chem.*, **116**, 401 (1925); Freundlich: "New Conceptions in Colloidal Chemistry," Dutton and Company, New York.

<sup>37</sup> Stern: *Z. Elektrochem.*, **30**, 508 (1924).

mium electrode that the charge of the cadmium surface must be negative for all possible concentrations of Cd-ions if the cadmium zero point coincides with the mercury zero point. But if we suppose that the cadmium zero point is shifted in the direction indicated by the experiments with Cd-amalgams quoted above by some 0.27 volt (the shift observed with a 4.8 per cent amalgam being 0.19 volt), the cadmium surface in a normal KCl solution would be positively charged even if the concentration of Cd-ions is as low as  $3.10^{-5}$  normal.

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# DETERMINATION OF THE NUMBER OF FREE ELECTRIC CHARGES ON AIR BUBBLES AND OIL DROPLETS DISPERSED IN WATER CONTAINING A SMALL AMOUNT OF CETYL SULFONIC ACID

BY JAMES W. MCBAIN AND ROBERT C. WILLIAMS

EVIDENCE is accumulating for the view that the double layer as envisaged by Helmholtz is not responsible for electrokinetic effects, but that they are caused by the unbalanced electrical charges upon the interface corresponding to free mobile ions of opposite sign which exist independently within the solution. It therefore becomes of increased importance to measure the number of free unbalanced charges upon a given interface.

One of us (R. C. W.) conceived the idea of using as a means for measuring the charge on any coarsely dispersed material (air bubbles, oil droplets or dense particles) in liquid media, a method analogous to that used by Millikan when determining the electronic charge with oil droplets in air. The method is to balance the natural tendency of the dispersed material to rise or fall under the influence of gravity by the application of a counter electromotive force. A direct measurement of the charge on the particle results from a knowledge of the gravitational force on the particle and the potential gradient.

To date no previous studies using such a null-point method have been reported in the literature. Modifications of the idea have been indicated. Burton,<sup>1</sup> in some studies of particle size, has suggested the use of a potential greater than that necessary to prevent natural rise or fall of the dispersed material. However, for the measurement of the charge on a particle, the null-point method is incomparably more satisfactory and very simple. The most interesting and valuable work done on the charges on air bubbles of nearly the same size as those investigated here is that of McTaggart,<sup>2</sup> Alty,<sup>3</sup> and Currie and Alty.<sup>4</sup> They used electrophoresis experiments with a highly specialized technique very restricted in its range of application.

<sup>1</sup> Proc. Roy. Soc., London, **95** A, 480 (1919).

<sup>2</sup> Phil. Mag. (6), **27**, 297 (1914); (6), **28**, 367 (1914); (6), **44**, 386 (1922); Trans. Roy. Soc., Can., **18**, III, 129 (1924).

<sup>3</sup> Proc. Roy. Soc., London, **106** A, 315 (1924); **110** A, 178 (1926).

<sup>4</sup> Proc. Roy. Soc., London, **122** A, 622 (1929).

## I. EXPERIMENTAL

The solution (always N/10,000 cetyl sulfonic acid) was placed in a vertical test tube of 7 mm. bore provided with a side arm sloping diagonally upward to the same height as the top of the test tube. One carbon electrode reached down the side arm nearly to the junction, and another was inserted at the top of the test tube so that the ends immersed in the solution were but 3 cm. apart. Gases evolved by the slight electrolysis therefore escaped from the top of the solution without disturbing that under observation between the electrodes. 110 volts d.c. and 40 volts d.c. were used in these experiments.

The suspended particles or bubbles were observed through a telescope with a calibrated micrometer eyepiece (Cambridge Instrument Co.) provided with adjustable cross wires.

## METHOD

The bubbles or droplets were suspended in water (containing 0.0001 N<sub>w</sub> cetyl sulfonic acid to stabilize them) by shaking with air or benzene. The coarse dispersion was then poured into the tube, the electrodes were placed, and observations were made of the suspension at a point half-way between the electrodes.

At any time after the fast-moving, large bubbles or droplets had risen to the surface, there were at most no more than five or six in the field. The movement of a single bubble was therefore readily followed, and the effect of the applied potential was observed.

When a bubble or droplet started across the field, it was timed over a distance of 1.5 mm., for example, after which time the potential was applied and its effect was observed. The timing of the bubble over a known distance enabled the calculation of its size to be made, using a modification<sup>5</sup> of Stokes' law. The size was also estimated when the particle was stopped or when it moved slowly, under the influence of the potential, in the field of the telescope by aid of the calibrated scale and micrometer adjustment.

The estimation of the size of the particles by use of the modification of Stokes' law was not of great accuracy because the time required for the particle to travel the distance between the cross-wires was very short. However, the values checked, in general, quite well with those made by direct estimation of the diameter using an ocular micrometer.

The response of the bubble or droplet to the applied potential was practically instantaneous, whether to stop it, decrease its speed, increase

<sup>5</sup> Burton: "Physical Properties of Colloidal Solutions," Longmans, Green & Co., London, 126 (1916).

its speed, or reverse its direction, depending on its size and the signs of the electrodes. It was possible to keep a particle in the field for some time, provided that it was sufficiently small to be reversed in direction by the potential.

Streaming effects of the liquid near the wall of the tube were apparent, but the telescope was focused on particles in the center of the tube when recorded observations were made. It appears unlikely that any general streaming vitiated the results because of the following considerations: (1) the lack of hysteresis of the particles when the potential was applied; (2) the focusing of the telescope well away from the wall; (3) the lack of other than straight motion of the particles under the influence of the potential; (4) the lack of mass sweeping of large and small particles; and (5) the comparatively sharp dividing line in size distribution of those which responded definitely in one way to the potential.

### RESULTS

About 100 observations and measurements were recorded using air bubbles and benzene droplets. A few qualitative experiments were made using a fine clay. The tables give typical results for given sets of conditions.

TABLE 1.—AIR BUBBLES IN 0.0001  $N_w$  CETYL SULFONIC ACID SOLUTION

110 volts; electrodes 3 cm. apart; potential gradient 36.6 volts/cm. or 0.122 electrostatic units/cm. Bubbles timed over a distance of 1.5 mm. Average size of bubbles stopped: observed radius 0.0015 cm.; calculated radius 0.00152 cm.

Time of the Natural Rise, in Seconds, for Bubbles of Graduated Sizes	Effect on Applying the Electric Field
1.3	Motion still upwards
1.4	Motion still upwards
1.7	Motion still upwards
1.9	Motion still upwards
2.2	Motion still upwards
2.5	Motion still upwards
2.6	Motion stopped
2.8	Motion stopped
3.0	Motion stopped
3.3	Motion stopped
4.3	Motion downwards (reversal)
4.5	Motion downwards (reversal)
4.8	Motion downwards (reversal)

TABLE 2.—AIR BUBBLES IN 0.0001 N<sub>W</sub> CETYL SULFONIC ACID SOLUTION

40 volts; electrodes 3 cm. apart; potential gradient 0.0443 electrostatic units/cm. Bubbles timed over a distance of 1.5 mm. Radius of bubbles stopped: observed 0.001 cm.; calculated 0.0011 cm.

Time of Natural Rise in Seconds for Bubbles of Graduated Sizes	Effect on Applying the Electric Field
3.0	Motion still upward
3.5	Motion still upward
5.0	Motion stopped
6.5	Motion stopped
8.0	Motion downward (reversal)
13.0	Motion downward (reversal)

$$r^2 = \frac{9}{2} \cdot \frac{(0.01)(0.027)}{(1.0 - 0.001)(980)} = 0.00000125; r = 0.0011 \text{ cm.}$$

Average velocity = 0.027 cm./sec.

TABLE 3.—BENZENE DROPLETS IN 0.0001 N<sub>W</sub> CETYL SULFONIC ACID SOLUTION

110 volts; potential gradient 0.122 electrostatic units/cm. Bubbles timed over a distance of 1.5 mm. Radius of droplets stopped: observed 0.005 cm.; calculated 0.0041 cm.

Time of Natural Rise in Seconds for Droplets of Graduated Sizes	Effect on Applying the Electric Field
1.5	Motion still upward
2.5	Motion still upward
3.0	Motion still upward
3.0	Motion stopped
3.5	Motion stopped
3.7	Motion stopped
4.5	Motion downward (reversal)
4.7	Motion downward (reversal)
5.0	Motion downward (reversal)

$$r^2 = \frac{9}{2} \cdot \frac{(0.01)(0.044)}{(1.0 - 0.88)(980)} = 0.0000168; r = 0.0041 \text{ cm.}$$

Average velocity = 0.044 cm./sec.

The calculation of the size of the bubble by the appropriate formulation of Stokes' law is as follows:  $r^2 = \frac{9}{2} \frac{\eta v}{(s - s')g} = \frac{9}{2} \frac{(0.01)(0.05)}{(1 - 0.001)(980)}$   
 $= 0.0000023$  cm.;  $r = 0.00152$  cm.; where  $\eta$  is the viscosity of the solution,  $s$  and  $s'$  are the densities of the water (solution), and the particle  $g$  is the gravitational constant, and  $v$ , the velocity in cm./sec. (average of many observations),  $= 0.05$  cm./sec.

#### CALCULATION OF THE CHARGES ON THE AIR BUBBLES AND BENZENE DROPLETS NEGLECTING THE ELECTRICAL DRAG OF THE FREE MOBILE IONS

In order to make these calculations it was necessary to equate<sup>6</sup> the electrical pull  $F \cdot e_n$  with the "gravitational" pull  $mg$ , where  $m$  is the mass of the particle,  $g$  the gravitational constant,  $F$  the electric field in e.s.u./cm., and  $e_n$  is the electric charge in e.s.u. The product  $mg$ , expressed in dynes, equals  $\frac{4}{3} \pi r^3 (s - s')g$ , where  $r$  is the radius of the particle,  $s$  the density of the solution,  $s'$  the density of the particle, and  $g$  the gravitational constant.

*Calculation I, for Table 1:*  $mg$ , for the air bubble considered, therefore  $= \frac{4}{3} \pi (0.0015)^3 (1.0 - 0.001) 980 = 0.00001384$  dyne. This factor may also be calculated by the use of Stokes' law,  $mg = 6 \pi r \eta v$ . The electrical field expressed in e.s.u./cm. is

$$\frac{110 \text{ (volts)}}{3 \text{ (cm.)}} (0.00333) = 0.122$$

$$(3.33 \times 10^{-3} \text{ e.s.u.} = 1 \text{ volt}).$$

Therefore,

$$e_n = \frac{0.00001384}{0.122} = 1.13 \times 10^{-4} \text{ e.s.u.},$$

or,

$$\frac{1.13 \times 10^{-4}}{4.774 \times 10^{-10}} = 2.4 \times 10^5 \text{ electronic charges.}$$

The number of possible charges, assuming a completely dissociated monomolecular film of soap on the bubble and that the "area"<sup>7</sup> of each is  $20.3 \times 10^{-16}$  sq. cm., would be

$$\frac{28 \times 10^{-6}}{20.3 \times 10^{-16}} = 1.38 \times 10^{10}$$

<sup>6</sup> Millikan: "The Electron," Chicago, University of Chicago Press (1917).

<sup>7</sup> Langmuir: J. Am. Chem. Soc., **39**, 1848 (1917).

*Calculation II, for Table 2:* Considering the air bubble of Table 2 (radius 0.001 cm.),

$$mg = \frac{4}{3} \pi (0.001)^3 (1.0 - 0.001) 980 = 0.0000041 \text{ dyne.}$$

$$F \text{ (electric field)} = \left(\frac{4}{3}\right) (0.00333) = 0.0443 \text{ e.s.u./cm.}$$

$$e_n = \frac{0.0000041}{0.0443} = 9.3 \times 10^{-5} \text{ e.s.u.,}$$

or,

$$\frac{9.3 \times 10^{-5}}{4.774 \times 10^{-10}} = 1.95 \times 10^5 \text{ electronic charges.}$$

Number of possible charges (as above) would be

$$\frac{12.6 \times 10^{-6}}{20.3 \times 10^{-16}} = 6.2 \times 10^9$$

*Calculation III, for Table 3:* Considering the benzene droplet in Table 3 (radius 0.0041 cm.),

$$mg = \frac{4}{3} \pi (0.0041)^3 (1.0 - 0.88) 980 = 0.000034 \text{ dyne.}$$

$$F = \left(\frac{4}{3}\right) (0.00333) = 0.122 \text{ e.s.u./cm.}$$

$$e_n = \frac{0.000034}{0.122} = 2.8 \times 10^{-4} \text{ e.s.u.,}$$

$$\frac{28.0 \times 10^5}{4.774 \times 10^{-10}} = 5.9 \times 10^5 \text{ electronic charges.}$$

Number of possible charges (as above) would be

$$\frac{21.0 \times 10^{-5}}{20.3 \times 10^{-16}} = 1.03 \times 10^{11}$$

TABLE 4.—NUMBER OF ELECTRONIC CHARGES FOUND ON THE SURFACE OF A SINGLE BUBBLE OR DROPLET COMPARED WITH NUMBER WHICH COULD BE CLOSE PACKED IN MONOMOLECULAR LAYER OF FATTY IONS.

Particle	Radius in Centimeters	Area, Cm. <sup>2</sup> × 10 <sup>5</sup>	Charges Orthodox	Surface Covered, Per Cent
Air.....	0.001	12.6	$1.95 \times 10^5$	0.0031
Air.....	0.0015	28.0	$2.4 \times 10^5$	0.0017
Benzene.....	0.0041	210.0	$5.9 \times 10^5$	0.0006



Currie and Alty,<sup>8</sup> since this work was done, found by a similar calculation a charge of  $5.4 \times 10^{-4}$  e.s.u., or  $11.3 \times 10^5$  electronic charges on much larger air bubbles of 0.033 cm. radius in pure water by observing the rate of motion in a horizontal tube rotating on its axis and setting the electrical force equal to the friction calculated from Stokes' law. Bubbles of greater radius possessed no greater charge. The radii of the bubbles tested were all much larger than those in the null-point experiments.

## II. SUPPLEMENTARY ELECTROPHORESIS EXPERIMENTS WITH BENZENE DROPLETS

It was desirable to correlate the effect of the potential when acting in opposition to the rise of the droplet, in the null-point experiments, with the effect of the potential when acting at right angles to the natural vertical rise of the droplet.

This was done as follows: A suspension of benzene droplets was put into a tube ( $1.4 \times 9$  cm.) which was clamped in a horizontal position. The ends of the tube were closed by corks through which carbon electrodes were thrust. McTaggart<sup>9</sup> and Alty<sup>10</sup> rotated a similar tube to keep air bubbles in the center by centrifugal force. The droplets observed here were too small to be observed on account of irregularities in motion of the tube when rotation was attempted. It was therefore decided to allow the droplets to rise naturally and at the same time apply the potential. This procedure caused the droplet to take a course determined by the resultant of the two forces, namely, gravity and the electric field. Since the horizontal velocity due to the potential is the same whether or not the vertical force of gravity is acting, it was possible to obtain the velocity of the droplet by measuring the time required for it to rise from one cross-hair to the other whilst observing the horizontal component of its motion.

Using 110 volts with the electrodes 3 cm. apart and a droplet having a radius of about 0.004 cm., the time required for the droplet to go from one cross-hair to the other (1.5 mm. apart) was about 4 seconds. This corresponds within experimental error with the time required for a droplet of the same radius to rise naturally 1.5 mm. In the null-point experiments the velocity of natural rise might be looked upon as being neutralized by the tendency toward equal velocity in the opposite

<sup>8</sup> Proc. Roy. Soc., London, **122** A, 622 (1929).

<sup>9</sup> Phil. Mag. (6), **27**, 297 (1914); (6), **28**, 367 (1914); (6), **44**, 86 (1922); Trans. Roy. Soc., Can., **18**, III, 129 (1924).

<sup>10</sup> Proc. Roy. Soc., London, **106** A, 315 (1924); **110** A, 178 (1926); **122** A, 622 (1929).

direction as shown by the horizontal velocity produced by the potential. Consequently general streaming effects must be the same in each case if they are of sufficient magnitude to be detected by observation. As in the null-point experiments the telescope was focused well away from the wall of the tube so as to avoid streaming effects near the wall. The response in either direction to the potential, depending on the sign of the electrodes, was similarly sharply defined. Air bubbles of suitable size for observation move too rapidly to be measured by this method.

The most general experimental method suggested by the present null-point method is to weigh the electrical pull of the unbalanced charges on a solid or surface in an electrical field by means of a sensitive balance. A description of a robust null-point microbalance of the highest degree of sensitivity, suitable for this purpose, is being communicated by McBain and Tanner to the Royal Society (London).

### III. GENERAL CONCLUSION AND REVISION OF THE INTERPRETATION AND CALCULATION OF ELECTROKINETIC PHENOMENA

We have used the orthodox mode of calculation employed by Millikan and adopted by Currie and Alty.<sup>11</sup> The conclusion, that only a few millionths of the area of the surface of a bubble or droplet possesses a free charge on which an electric field exerts a pull, shows irresistibly, as Currie and Alty have pointed out, that the conceptions and formulations of Helmholtz are inapplicable. The results go further, for they thus carry within themselves a clear indication that this mode of calculation by which they were obtained is inadequate in view of the above conclusion.

In Millikan's experiments the calculation is valid because there were only negatively charged droplets and electrons present. In aqueous media, such as ours and Alty's and colloidal solutions in general, the system as a whole is neutral, and every free charge on a particle or interface is balanced by an ion of opposite sign somewhere within the system. The proper treatment of this subject is intrinsically connected with that in a general dissociation theory of electrolytes. A colloidal particle or bubble differs only in degree in its behavior from that of a true electrolytic ion as is clearly exhibited in the general formulation of Miss Laing.<sup>12</sup> Her experiments indicated that movement with respect to the solvent is independent of any mechanical restraint; for instance, it was identical for electrophoresis and electrosmosis.

In the present experiments the water is not at rest with respect to

<sup>11</sup> Proc. Roy. Soc., London, **122** A, 622 (1929).

<sup>12</sup> J. Phys. Chem., **28**, 673 (1924).

the bubble because of the electrical pull of the free mobile ions of opposite sign. The electrical pull caused by 1 volt per centimeter is  $1.592 \times 10^{-12}$  dynes per electronic charge of either sign and 964,752 kilograms for 1 gram equivalent of any charges whether on ions or interfaces. In ordinary electrolysis, despite the magnitude of these forces, they are exactly equal on the two ions, and the water remains at rest. When, as in the present experiments or electrosmosis, any mechanical force is superadded, the water must move correspondingly. Similarly, the drag of the opposite ions must always be taken into account when interfaces are moved through water; *e.g.*, a rising bubble, streaming potential, or Dorn effect. Altogether, electrokinetic experiments as at present evaluated therefore give minimum values for the charges.

Of other attempts to evaluate the number of unbalanced charges or free mobile ions, the experiments of Wintgen and Varga<sup>13</sup> are vitiated, as has been previously pointed out,<sup>14</sup> by ignorance of the fact that migration data obtained by the Hittorf method and the method of moving boundaries give identical data, merely expressed in different units, which cannot, therefore, be made use of as simultaneous equations. Such results, which are merely due to confusion of units, are of necessity illusory.

A completely different mode of measurement, almost free from ambiguity, is illustrated by the experiments by McBain and Peaker,<sup>15</sup> in which the number of mobile ions yielded by a monomolecular film of insoluble fatty acid on water, have been measured by their conductivity, showing that about one-ninth of the close-packed monomolecular film consists of fatty ions instead of molecules.

These and other similarly high results which we have obtained by the conductivity method for the number of electrical charges on various interfaces reinforce the consideration expressed in the third paragraph of the present discussion. In the usual evaluation only the frictional resistance of the bubble or droplet to movement through the system as a whole is taken into account, the bubble carrying or dragging with it its atmosphere of opposite ions practically as a whole. If, however, most of the shear is confined to layers of solvent between the charges of opposite sign, the frictional resistance may be far greater, and the number of charges necessary to effect this movement would be correspondingly multiplied.

<sup>13</sup> Kolloidchem. Beihefte, **11**, 1 (1919); Wintgen: Z. physik. Chem., **103**, 238 (1923); **107**, 403 (1924); Zsigmondy: "Kolloidchemie," 5th Ed., 173-193 (1925).

<sup>14</sup> McBain: Colloid Symposium Monograph, **4**, 1 (1926); Kolloid-Z., **40**, 1 (1926).

<sup>15</sup> Communicated to the Royal Society (London).

## SUMMARY

1. A simple null-point method for balancing electrophoresis of bubbles and droplets against gravitational rise or fall has been devised and found practical. The results check closely with those expected from Stokes' law when the two movements are observed at right angles to each other. A more general method is indicated employing a micro-balance.

2. It is clearly shown that the number of electronic charges, deduced in the orthodox way, occupy such an infinitesimal proportion of the surface that the classical treatment of electrokinetics on the basis of a double layer is invalid. It follows that a more general treatment corresponding to the electrochemistry of electrolytes is necessitated.

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# THE ELECTROSTATICS OF FLOTATION

BY H. B. BULL

THE purpose of this research was to investigate the electrostatic charge carried by finely ground galena particles in distilled water and in solutions of different concentrations of salts in the hope of being able to give a more logical and certain interpretation to the observed "toxic" effects of these salts on the flotation of galena.

As is well known, there is a quite definite relationship between the concentration of a salt added to a flotation circuit and its toxic effect. This is clearly shown by the work of Gaudin and his associates<sup>1</sup> and by

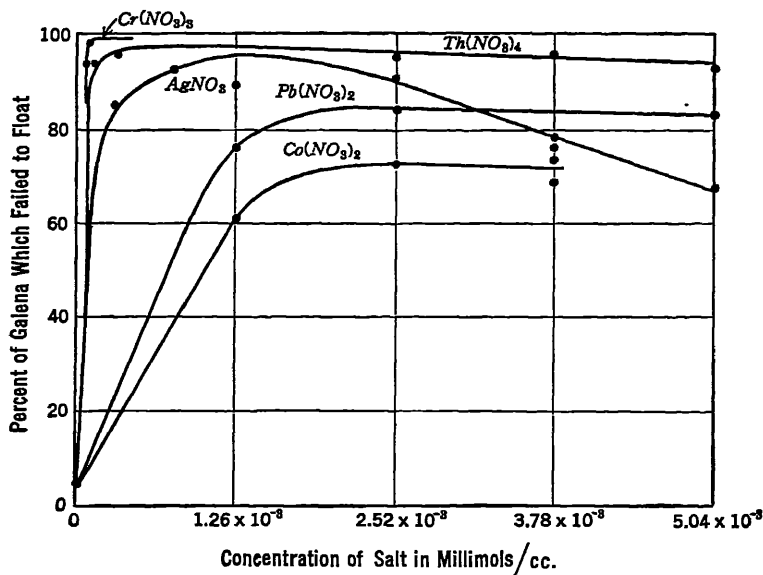


FIG. 1.

Taylor and Bull.<sup>2</sup> Figure 1 shows the typical effects of a number of cations on the flotation of galena.

An attempt was made to determine the electrostatic charge on finely ground galena with the streaming potential method in an apparatus

<sup>1</sup> Gaudin, Glover, Orr, and Hansen: "Flotation Fundamentals."

<sup>2</sup> J. Phys. Chem., **33**, 641 (1929).

developed by Briggs.<sup>3</sup> But the resistance of the galena was so low that no difference of potential could be observed.

The method finally adopted was based on a phenomenon discovered by Dorn<sup>4</sup> in 1878, and bearing his name. He found that when a body falls through a liquid there is a difference of electrical potential established between the top and bottom of the liquid. Stock<sup>5</sup> has clearly shown this difference of potential to be due to what is termed the zeta potential, that is, the difference in electrical potential which exists across the immovable adsorbed layer of ions and the boundary layer of movable molecules.

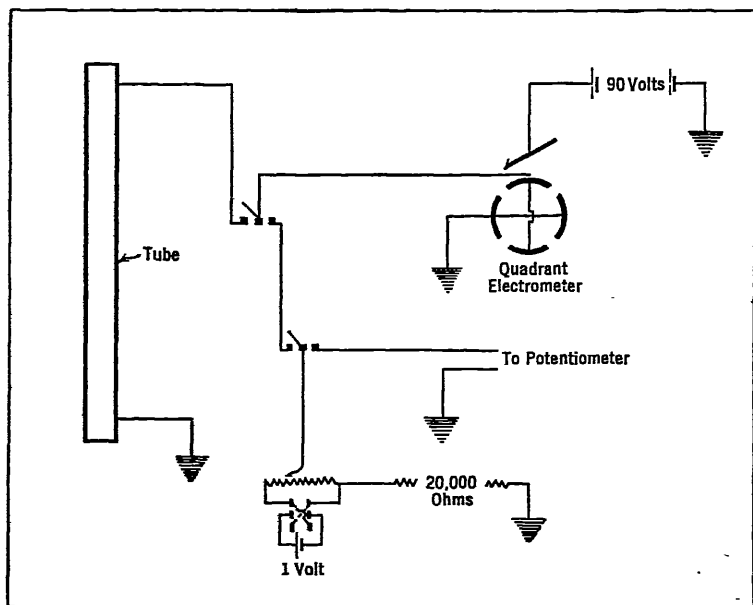


FIG. 2.

The actual experimental technique was to allow 10 gm. of the purest crystallized galena, which had been ground to pass a 100-mesh sieve and retained on a 325-mesh sieve, to fall through a glass tube 65 cm. long and 3 cm. in diameter, which contained the liquid in question. (See Fig. 2.) Platinum wires fused into the walls of the glass tube 2 cm. from each end were used as electrodes. A quadrant electrometer was used to register the difference of potential between the top and bottom of the tube. The observed deflection of the quadrant electrometer, produced by the

<sup>3</sup> J. Phys. Chem., **32**, 641 (1928).

<sup>4</sup> Dorn: Ann. Physik., (4) **3**, 20 (1878); **9**, 513; **10**, 46 (1880).

<sup>5</sup> Anz. Akad. Wiss. Wien, 131 (1913).

falling of the galena, was reproduced by an electromotive force whose strength could be accurately determined and thus the difference of potential produced by the falling galena was obtained.

The galena was allowed to fall through varying concentrations of the nitrates of Th, Cr, Ag, Pb and Co.

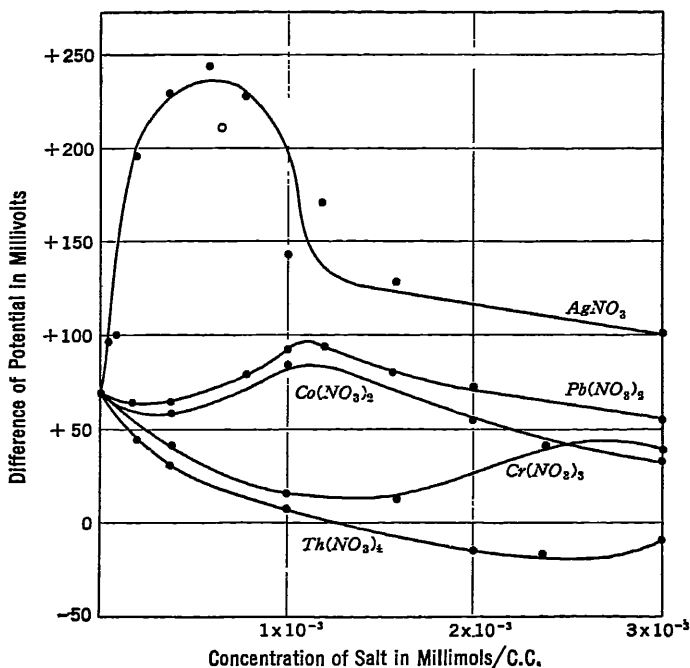


FIG. 3.

## RESULTS

In Fig. 3 the observed difference of potential is plotted as the ordinate against the concentration of the salt added in millimols per milliliter as the abscissa. The sign of the electrostatic charge on the galena is indicated. The results obtained for silver, cobalt and lead were rather consistent and it is believed that the values shown fairly represent the behavior of these salts; thorium and chromium were quite erratic and little faith can be placed in the values given, but I believe that the general shape and position of the curve is correct.

## DISCUSSION

It is clear that in this series of determinations the zeta potential has not been actually determined, but we have reason to believe that while

the difference of potential between the top and bottom of the liquid is not equal to the zeta potential it is, within certain limits, proportional to it.

A comparison between the toxic effect of Ag, Pb, and Co and the effect that these ions produced on the electrostatic charge of the galena is highly suggestive. It indicates, perhaps, that a large part of the toxic effect of these ions is due to the raising of the electrical charge on the particles of galena and so preventing them from collecting on the air bubble, thereby reducing the yield in flotation. This explanation becomes more convincing in the light of Burton and Currie's work,<sup>6</sup> who found that when small lead shot were dropped through solutions of salts of different concentrations there was a marked repulsion between the shot at certain salt concentrations as evidenced by scattering of the shot as they fell, and that these concentrations correspond to salt concentrations where there was a maximum difference of potential between the top and bottom of the liquid.

The reason for the large effect of the silver ion as compared with the lead and cobalt ion is probably due to the fact that the silver ion is absorbed to a much greater degree than the lead and cobalt ion, this greater adsorbability being due to the fact that silver sulfide is three times more insoluble than lead sulfide and eighty times more insoluble than cobalt sulfide.

Inasmuch as neither thorium nor chromium form stable sulfides and since the galena carries an initial positive charge, the nitrate ion in these cases plays a predominating rôle. There is apparently no connection between the extreme toxic effect of these ions on flotation and the electrostatic charge carried by the galena while in a solution of these salts.

It is also highly suggestive that finely ground quartz was found to carry a relatively large negative charge while it is well known that air bubbles in water are also negatively charged.<sup>7</sup>

### SUMMARY

1. There is an apparent connection between toxicity of Ag, Pb, and Co on the flotation of galena and the electrostatic charge carried by finely ground galena in solution of the nitrates of these cations.

2. There is apparently no connection between the toxicity of Th and Cr on the flotation of galena and the electrostatic charge carried by finely ground galena in solution of the nitrates of these cations.

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<sup>6</sup> Phil. Mag., (6) 49, 194 (1925).

<sup>7</sup> McTaggart: Phil. Mag., (6) 27, 297 (1914).



# SOME EVIDENCE ON THE NATURE OF EXTRA-MOLECULAR FORCES

BY DONALD H. ANDREWS

ONE of the outstanding problems of colloid chemistry today is the question of the depth of the adsorbed layer on crystal surfaces, whether it is uni- or poly-molecular. The purpose of this paper is to throw some light on this problem by presenting evidence on the nature of the forces which surround the molecule or, briefly, the extra-molecular forces as they are seen in experimental and theoretical studies of atomic and molecular vibration. The fact that there seems to be a very definite limit to the distance in space over which these forces operate puts a limit on the number of molecular layers which can be held by purely chemical forces emanating from the surface of a crystal. It is, of course, true that we may have electrical forces operating particularly with polar compounds, and that a surface may induce other forces in the molecules which it adsorbs, and that these might explain the adsorption of still further layers. It should, however, be one step in simplifying the problem if we could decide over what range in space the purely chemical forces can operate directly. This is the question on which this paper presents some evidence.

## I. EVIDENCE FROM SPECIFIC HEATS

The first evidence to be presented here on the nature of extra-molecular forces was brought to light in a study of the specific heats of crystalline organic compounds.<sup>1</sup> The connection between specific heat and the field of force around the molecule may be seen by considering the nature of thermal energy. In a crystal of benzene, for example, the thermal energy will be made up of several different parts. There will be the energy of motion of the carbon and hydrogen atoms vibrating under the restraint of the chemical bonds, and there will also be the energy in the vibratory motions of the benzene molecules themselves regarded as units in the crystal lattice. Now the frequency of vibra-

<sup>1</sup> Andrews: Proc. Roy. Acad., Amsterdam, 29, 744 (1926); Chem. Reviews, 5, 533 (1928).

tion ( $\nu$ ) in such cases will depend on the mass ( $m$ ) of the particle vibrating and on the force ( $k$ ) restraining it according to the equation

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}. \quad (1)$$

Thus in the case of benzene the frequency of vibration of the hydrogen atoms is found to be about  $8.95 \times 10^{13} \text{ sec}^{-1}$ , and that of the carbon atoms of the order of  $3.03 \times 10^{13} \text{ sec}^{-1}$ . On the other hand, the frequency of the vibration of the molecule as a whole, acting as a unit in the crystal lattice, is much lower, having a value of  $0.33 \times 10^{13} \text{ sec}^{-1}$ .

As the quantum theory has shown, it is the values of these frequencies which determine the temperature at which the specific heat disappears when the temperature of the crystal is lowered. In the case of benzene and most other organic molecules, the above values of the frequency lead to a kind of freezing of the molecule at about  $100^\circ \text{ K}$ . In other words the frequencies of the internal vibrations are so high, resulting in such large quanta, that the molecule at  $100^\circ \text{ K}$  will not contain any appreciable amount of internal vibrational energy.<sup>2</sup>

On the other hand, considering the molecule moving as a whole as a unit in the crystal lattice, the frequency is low enough so that there is still a comparatively large energy of vibration at this temperature. We thus have an ideal case for studying the action of the forces around the molecule, because we are dealing with a molecule which has become, in effect, a rigid body, its only energy being that of vibration under the influence of the field of force which surrounds it. In other words, the extra-molecular force may be studied through its effect on the frequency of vibration.

For a crystal lattice where the unit is an individual atom and not a molecule, Lindemann has shown that<sup>3</sup> there is a relation between the frequency of vibration ( $\nu$ ) of the atom and the melting point ( $T_m$ ) atomic volume ( $V$ ) and atomic weight ( $M$ ) as follows:

$$\nu = 3.08 \times 10^{12} \sqrt{\frac{T_m}{MV^{2/3}}} \quad (2)$$

This is based on the idea that at the melting temperature the atom must possess energy just sufficient to make its amplitude of vibration equal to the average distance between the atoms. Thus we see the two-thirds power of the atomic volume entering into the expression

<sup>2</sup> Excepting the zero-point energy which does not enter into the specific heat.

<sup>3</sup> Physik. Z., 11, 609 (1910). For the value of empirical constant see Nernst, "Vorträge über die kinetische Theorie der Materie und der Elektrizität," Göttingen (1914).

because this is equal to  $6.06 \times 10^{23}$  times the square of the distance between the units in the crystal lattice, the distance which is assumed to be the amplitude of vibration at melting.

In carrying over this idea to the problem of a crystal lattice where the unit is a *molecule* it is necessary to examine carefully the changes which must be made in order to apply a formula of this type. In general the mechanical problem will be about the same except that we now have a real solid body with both mass and moment of inertia as our vibrating unit instead of a point mass with no moment as in the atomic lattice. Each unit will therefore possess six degrees of freedom instead of three, and if no vibrations occurred inside the molecule we would expect the heat capacity of the lattice to approach at high temperatures a value twice the Dulong and Petit value.

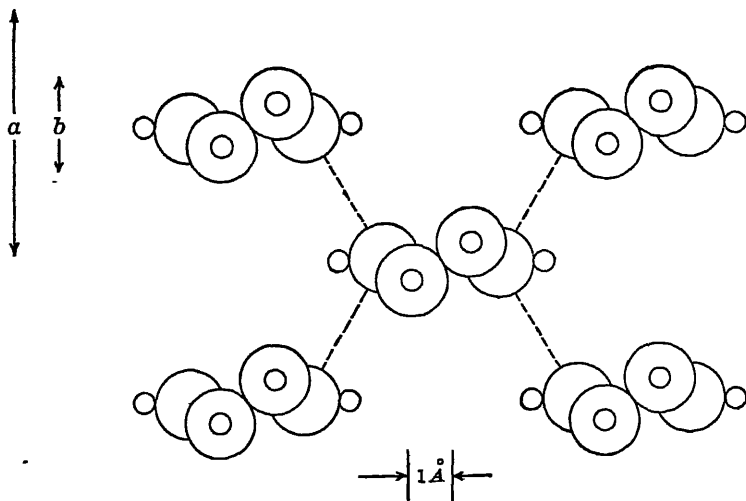


FIG. 1.—Benzene molecules arranged as in the crystal lattice. Approximate distance through which molecule will vibrate at melting temperature, distance corresponding to  $\theta = 45$  indicated by  $a$ ; to  $\theta = 159$ , by  $b$ .

However, in applying the formula to a molecular crystal lattice there seems to be only one factor in equation (2) which might need to be changed. The melting point ( $T_m$ ) is obviously unequivocal and the mass ( $M$ ) will be the mass of the molecule, but in selecting a value for ( $V$ ) the question is: should we assume that in melting the molecule really must vibrate with an amplitude equal to cube root of the volume it occupies in the lattice. It is this point which throws light on the nature of the field of force surrounding the molecule.

Taking benzene as an example, Fig. 1 shows the problem graphically.

The molecules are drawn as they would be placed in a cross-section of the benzene crystal lattice. The dotted lines represent a possible location of the crystal forces operating between the molecules in this cross-section. If, in equation (2), we use the molecular volume of benzene, it is equivalent to assuming an amplitude of vibration of  $5.2 \text{ \AA}$ , indicated by the distance marked  $a$  in the figure. This gives us a value for the frequency of 45, expressed in characteristic temperature units.<sup>4</sup> Now this can be used to calculate the molar heat capacity.

As was explained in a previous paragraph, at temperatures below  $100^\circ \text{ K}$  the heat capacity will depend solely on the frequency of vibration of the molecule-units in the crystal lattice, and since this, in turn, is given by equation (2) we see that in calculating heat capacity the only uncertainty lies in the value of the amplitude of vibration at melting. Figure 2 shows the values of the heat capacity calculated for

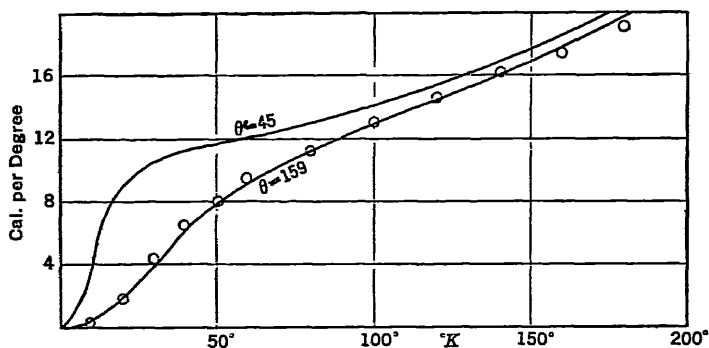


FIG. 2.—The heat capacity of crystalline benzene. The curves indicate calculated values; the circles, observed values.

$\theta = 45$  with the help of the formula of the quantum theory.<sup>5</sup> The circles represent the observed values of the heat capacity.<sup>6</sup> It is obvious that we do not have agreement, and we therefore consider why the amplitude at melting is probably smaller than  $5.2 \text{ \AA}$ .

In the first place we can interpret melting in terms of the field of force around the molecule. On that basis melting takes place when vibration separates two molecules so far that the restoring force is not sufficient to pull them together again. In other words, we think of the

<sup>4</sup> Since frequency always occurs in specific heat formulas as frequency multiplied by  $h$ , Planck's constant, it is customary to express it as  $\theta = h\nu/k$  which has the dimension of temperature.

<sup>5</sup> For the details of the calculation see Reference 1.

<sup>6</sup> Nernst: *Ann. Phys.*, **36**, 395 (1911).

restoring force as an attraction which is large when the molecules are about  $2 \text{ \AA}$  apart but very much smaller at, say,  $4 \text{ \AA}$  separation. The exact nature of this falling off is discussed in the next section.

The point to be made here is that we can account for the specific heat if we assume that the amplitude of vibration at melting is not of the order of a *molecular* diameter but of an *atomic* diameter. In other words, if we use for  $V$  in equation (2) the value of the molecular volume of *graphite*,  $5.32 \text{ cc.}$ , instead of that for benzene, we get a value of  $\theta = 159$ , which in the quantum formulæ gives the curve shown in Fig. 2. This curve, as contrasted with that for  $\theta = 45$ , is not only of the right shape but also fits the experimentally observed values, almost within their limit of error. This, therefore, appears to be strong evidence that the attractive force around the molecule falls off to very small values, insufficient to hold two molecules together, when the molecules have been displaced from their normal positions in the lattice by a distance comparable with the diameter of the carbon atom. The cube root of the molecular volume of graphite is shown as distance (b) in Fig. 1.

The same calculation has been made for all the other organic compounds for which the heat capacities have been measured in the range  $100^\circ \text{ K}$  to  $20^\circ \text{ K}$ . With but one exception quinhedrone, which is probably associated in the crystal state, the experimentally observed points are reproduced almost within the limit of error by using the value of  $V$  for graphite in equation (2), while the use of the actual molecular volumes gives quite erroneous results. It therefore seems that we have here a fairly correct picture of the way in which the extra-molecular forces operate. In the following section the values of the frequency, which we have secured in the manner just indicated, are employed in the wave mechanics formulae to give a more quantitative idea of the force.

## II. CHEMICAL FORCE IN WAVE MECHANICS

It has long been one of the outstanding problems of theoretical physics to secure a dynamical expression for the so-called chemical or valence force. We have known for some time that qualitatively this force acts like a spring operating between the two atoms which it joins. For example, the force joining a hydrogen atom to a carbon atom in a hydrocarbon, holds the hydrogen at a distance of about  $1 \text{ \AA}$  unit at equilibrium. If the hydrogen is pulled half an  $\text{\AA}$  further away there is a large force tending to pull it back, but if it is pulled  $2 \text{ \AA}$  away from its equilibrium position there is scarcely any restoring force, that is, the hydrogen is practically dissociated from the carbon.

Now the problem has been to get an exact expression for the way this force varies with distance. It must be, of course, an expression which is consistent with the spectroscopically observed energy levels and with the observed energy of dissociation.

The vibrational energy levels for diatomic molecules follow a very simple law:

$$E_n = E_e + hc\omega_0 \left(n + \frac{1}{2}\right) - hc\omega_0 x \left(n + \frac{1}{2}\right)^2 \quad (3)$$

$E_n$  being the energy in the  $n$ th vibrational state;  $E_e$  the electronic energy;  $h$  Planck's constant;  $\omega_0$  the fundamental frequency of vibration, in wave numbers;  $x$  a constant;  $c$  the velocity of light; and  $n$  the quantum number.

In the classical quantum mechanics this alone is not sufficient to tell how the force varies with the separation of the atoms but in the wave mechanics a solution is possible. Morse<sup>7</sup> has shown that the potential energy of such a diatomic oscillator with the above energy levels will be of the form

$$E_r = De^{-2a(r-r_0)} - 2De^{-a(r-r_0)} \quad (4)$$

where  $E_r$  is the potential energy at the distance of separation  $r$ ;  $r_0$  is the equilibrium distance of separation where there is neither attraction nor repulsion;  $D$  is the energy of dissociation; and  $a$  is a constant such that

$$a^2 = 8\pi^2 c \mu \omega_0 x h^{-1} \quad (5)$$

where  $c$  is the velocity of light;  $\mu$  the reduced mass of the vibrator; and  $\omega_0$  and  $x$  are the same as in equation (3).

There are two secondary relations which are also helpful:

$$D = \omega_0^2 / 4 \omega_0 x \quad (6)$$

and

$$r_0^3 \omega_0 = 3000 \text{ \AA}^3 / cm \quad (7)$$

Equation (7) is an empirical rule discovered by Morse which appears to be widely applicable for finding  $r_0$  from the fundamental frequency.

The expression in which we are most interested however is that for the variation of the force. This can be secured from equation (4) by differentiation giving

$$F = - \frac{dE_r}{dr} = 2aD (e^{-a(r-r_0)} - e^{-2a(r-r_0)}) \quad (8)$$

Now while Morse developed equation (4) for the case of a diatomic oscillator there is good reason for believing that we can use equation (8)

<sup>7</sup> Phys. Rev., **34**, 57 (1929).

for investigating how the attraction varies with separation for any atoms attracted by a chemical force. There is strong evidence that we are dealing with the same mechanism of attraction in all cases of homopolar valence because the force is always of about the same magnitude<sup>1</sup> whether we take the case of attraction between two very small atoms as in the hydrogen molecule, or whether we have a small and a large atom as in C—H, or two large atoms as in C—C.

Moreover, Morse's rule, equation (7), applies surprisingly well to cases where we can check  $r_0$  by means of X-ray measurements. It gives a distance of separation of 1.48 Å for C—C which checks that actually observed in the X-ray study of the diamond crystal lattice, 1.54 Å. In the case of benzene molecules where we would hardly expect it to apply at all, it gives 3.4 Å, while the X-ray data give a value of the order of 3.5 Å, so it seems worth while applying equation (8) to the forces which we think are involved in surface adsorption in the hope of throwing some light on their nature.

TABLE 1.—CONSTANTS USED IN CALCULATING FORCE CURVES

	C—H	C—C	(C <sub>6</sub> H <sub>6</sub> )... (C <sub>6</sub> H <sub>6</sub> )	
$D$	97.0	81.6	10.7	Cal.
$\omega_0$	3000	919	78.3	cm. <sup>-1</sup>
$M$	0.92	12	60	gm.
$a$	2.00	2.31	$1.21 \times 10^8$	cm. <sup>-1</sup>
$r_0$	1.00	1.54	$3.38 \times 10^8$	cm.

Table 1 contains the constants used in equation (8) for calculating the variation of the force in the C—C, C—H, and (C<sub>6</sub>H<sub>6</sub>)... (C<sub>6</sub>H<sub>6</sub>) bonds. The results are shown in Fig. 3. The circles represent the positions of the atoms at equilibrium distance where there is neither attraction nor repulsion. The curves show how rapidly enormous repulsion is built up if the atoms approach one another any closer than equilibrium, and how the attraction goes through a maximum as the atoms are pulled apart and then falls off quite rapidly. It is quite evident that the attraction has become almost negligible when the displacement from equilibrium is only 2 Ångstrom units.

As an application of these ideas let us consider the adsorption of benzene on a molecularly plane glass surface. The forces on such a surface should resemble very closely those on a diamond surface. If we think of these as being the bonds from the surface carbon atoms which

be unsatisfied, we can represent the field of force as shown in Fig. 4, where the density of the lines indicates the intensity of the attraction.

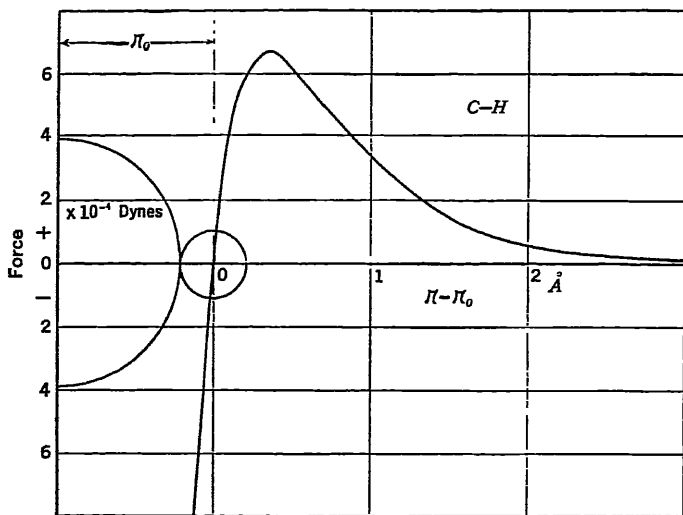


FIG. 3a.

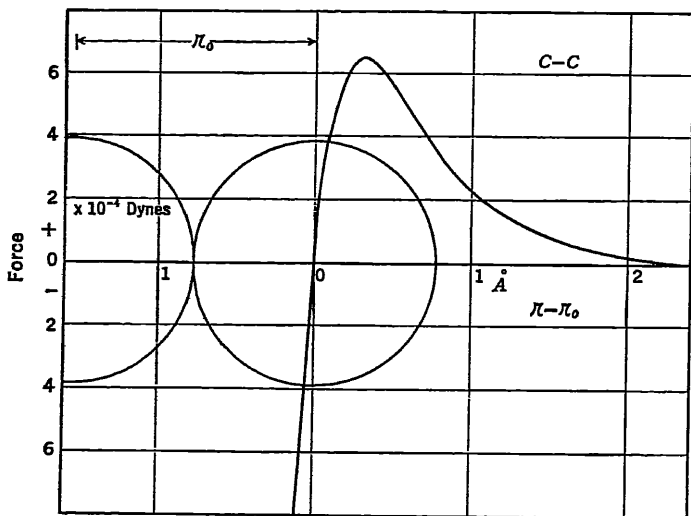


FIG. 3b.

FIGS. 3a and 3b.—The variation of the mechanical force of the chemical bond with distance; a for C-H; b for C-C.

Similarly the density of the dots around the benzene molecule indicates the intensity of the attractive force. It seems evident that if this picture



is correct, the purely chemical forces cannot possibly extend over a sufficient distance to produce a polymolecular adsorbed layer. The

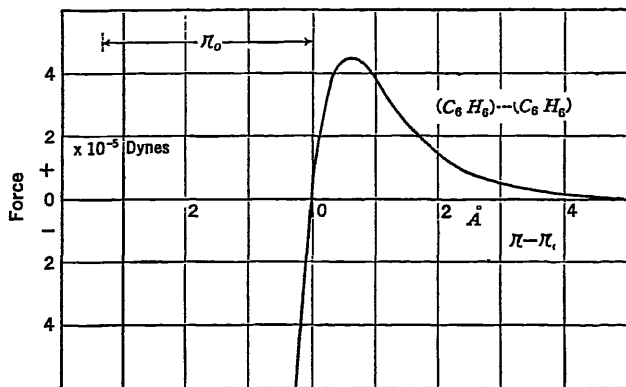


FIG. 3c.—The variation with distance of the intermolecular force between benzene molecules.

figure shows that beyond two Angstrom units the force is insufficient to hold a molecule to the surface. Thus while the first layer of adsorbed molecules is held very strongly in the neighborhood of 2 Angstrom units

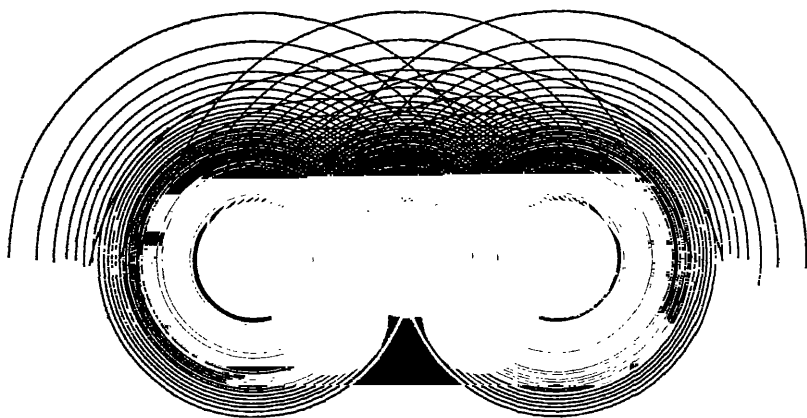


FIG. 4a.—Chemical force at a diamond crystal surface. The three upper black spheres represent the carbon atoms on the surface. The atoms in the interior are not filled in. The density of lines indicates the intensity of attraction.

from the surface, a second layer of adsorbed molecules which would have to be about 4 Angstrom units from the surface, would scarcely be attracted at all.

It might be reasoned that under these conditions the nature of the forces may be changed so that they will extend over larger distances.

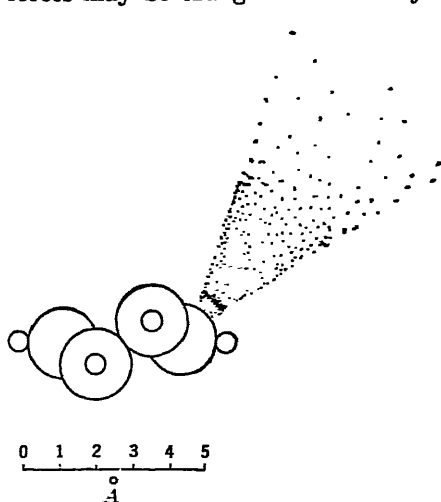


FIG. 4b.—Extra molecular force. The dots represent the intensity of attraction in a section of the field surrounding the benzene molecule.

tion goes to show that chemical forces do not extend much beyond an atomic diameter from the effective surface of an atom or molecule. This view favors the hypothesis of a unimolecular adsorbed layer.

Aside from there being little or no evidence in favor of such a phenomenon, one must bear in mind that the energy relation will always hold which makes the heat of adsorption equal to the integral of the force over the distance, as the molecule is brought up to the surface. If we should assume, as some have done, that these forces can extend ten or even a hundred times the distance shown in the figures, we should expect to have heats of adsorption many times those actually observed.

We may conclude then that the evidence from the study of atomic and molecular vibra-

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# THE ADSORPTION OF VAPORS

BY WALTER A. PATRICK

WHILE the conclusions of this paper are generally applicable to the adsorption of all vapors, the experimental portion will deal solely with the adsorption of water vapor by silica gel. Historically this problem plays an important rôle in the development of colloidal chemistry, for a consideration of the peculiar retention of water by the chemically inert but highly porous silica gel has led many noted chemists to conclusions that were at variance with the orthodox principles of physical chemistry. In fact it may be said that the explanation of this phenomenon was partially responsible for the creation of the new and separate division of colloid chemistry. Notwithstanding the years of experimentation beginning with Graham, we are still far from a final answer to the problem.

It is the purpose of this paper to mention briefly the experimental work preceding that of this paper and then to examine critically all of the experiments with a view of discovering the mechanism of the adsorption.

Graham, van Bemmelen, Anderson, and Zsigmondy by their work brought out the following facts:

1. Water is retained by silica gel in a non-stoicheiometrical manner.
2. A study of the variation of the amount of water retained with the equilibrium pressure of water over the adsorbent is a highly complicated function, exhibiting hysteresis, and certain discontinuities.
3. The rate of adsorption is extremely slow but may be accelerated by allowing the adsorption to take place in the absence of permanent gases.
4. The pores of the gel are ultra-microscopic—about  $5\ \mu\mu$  in diameter.
5. Ultra-microscopic observations of the partially dried gel exhibit a heterogeneity of approximately the same order of magnitude as above.

In this laboratory we have collected the following additional facts:

1. From heat of wetting measurements the surface of the gel may be calculated as  $6 \times 10^6\ \text{cm}^2$ .

2. The heat of wetting of water between  $0^{\circ}$  and  $4^{\circ}$  is positive.
3. The rate of adsorption of water vapor is slower than that of alcohol, benzene or carbon tetrachloride.
4. In a static method of measurement the presence of a small amount of permanent gas enormously retards the attainment of equilibrium; in fact, it prevents real equilibrium from ever being established.

These facts led to the following experiments, which were made by Drs. P. B. Davis and E. H. Barclay in the research laboratory of The

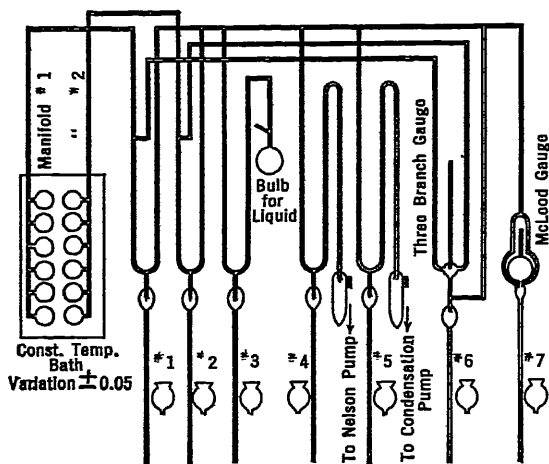


FIG. 1.

Silica Gel Co. These experiments were made with a view of obtaining equilibrium measurements of the adsorption of water vapor by silica gel. The essential feature of these measurements was the most rigid exclusion of all permanent gases from the adsorbent prior to making the adsorption measurements.

The operation of the apparatus will be apparent from Fig. 1. Temperatures were controlled to within  $0.05^{\circ}$  C. The vacuum pumps reduced the pressure to less than  $10^{-6}$  mm. The procedure in all cases was as follows:

1. Adsorbents activated at  $350^{\circ}$  C. *in vacuo* until no further gases were evolved.
2. Approximately 100 cc. of adsorbent introduced into each of twelve tared bulbs, weighed, and then sealed to the adsorption apparatus.
3. Boiled water introduced into "Bulb for liquid," Fig. 1.
4. Temperature of adsorbent raised to  $100^{\circ}$  C. and evacuated from ten to twelve hours.
5. Adsorbents shut off and water made "air free."
6. Adsorbents opened up to water bulb at room temperature. Operations 4 and 6 were repeated at *least three times*. The adsorbent and water were then in a completely air-free condition and the adsorption measurements could be made with the certainty of attaining true equilibrium.

The partial pressure of water vapor over the saturated gel was reduced somewhat by pumping. This pressure was accurately measured at the constant temperature. One of the bulbs was now sealed off and the water content determined by three different methods. A lower point on the adsorption curve was obtained by the further reduction of the partial pressure of water vapor, another bulb sealed off and the corresponding water content determined as above. After six points on the desorption curve were obtained, the partial pressure of water vapor over the remaining gel in the other bulbs could be gradually increased by exposure to the water bulb and the adsorption curve measured in the reverse manner.

The water content of the various gels was determined as follows:

First method: Differential weighing before and after heating to  $1000^{\circ}\text{C}$ . to constant weight.

Second method: Passing air dried with  $\text{P}_2\text{O}_5$  over the gel at  $1000^{\circ}\text{C}$ . and adsorbing the water in  $\text{P}_2\text{O}_5$ .

Third method: Differential weighing of bulbs made directly.

These three methods checked to within 1 per cent. The results of these experiments are shown in Fig. 2 where the grams of water adsorbed per gram of gel as ordinates are plotted against the equilibrium pressure of water vapor.

The absolute value of the adsorption is of slight theoretical significance inasmuch as this may be widely varied by changing the apparent density of the gel. This latter change is most readily brought about by controlling the temperature of the washing of the hydrogel.

It is to be noticed that these adsorption curves differ fundamentally from those found by van Bemmelen, Zsigmondy, and

Anderson. The first important difference is that there is not the slightest evidence of hysteresis, the adsorption and desorption curves coinciding completely. The other difference and, by far the most important, is the absence of any flex in the various curves. The preceding observers all found a relatively small adsorption at the low pressures which increased greatly after a certain supposedly definite pressure of water vapor was reached. This region of large adsorption at relatively constant pressure was sup-

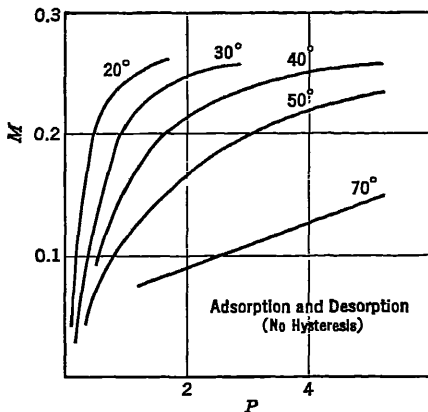


FIG. 2.

posed by Zsigmondy to mark the beginning of capillary adsorption. The same view is expressed by Hückel in his recent book on adsorption, whereby capillary condensation is distinguished from some other kind of adsorption upon the evidence of the experimental studies of the silica gel-water system. It cannot be too strongly emphasized that this conclusion is based upon erroneous experimental results. The discontinuities of the earlier workers are due entirely to the presence of permanent gases during the adsorption measurement which, by interfering with the wetting, produce pseudo equilibria.

The results of these experiments as summarized in Fig. 2 present a number of difficulties in finding a suitable mechanism of adsorption. The various methods of explaining the retention of water by silica gel may be stated as follows:

1. Chemical combination resulting in the formation of a series of hydrates.
2. A monomolecular layer covering either partially or entirely at saturation the vast surface of the gel.
3. A polymolecular layer that increases in thickness as the partial pressure of the water vapor is increased.
4. Filling of the capillary spaces, the equilibrium pressure over the gel increasing as the curvature of the water in the capillaries decreases.

The first explanation was abandoned years ago, due to the fact that chemically inert liquids such as hydrocarbons behave towards silica gel in the same manner as water.

The monomolecular layer theory is insufficient to explain the magnitude of the total adsorption even when the internal surface of the gel is assumed to be as great as  $6 \times 10^6$  cm.<sup>2</sup> per gram of gel.

The polymolecular layer theory could easily explain the entire behavior of the system, but experiments made in this laboratory have proven that on a plane surface the adsorbed water layer is not thicker than a monomolecular layer.

There remains the capillary condensation theory. The most serious objection to the application of this theory is that in its present form capillary spaces of less than molecular in diameter must be assumed to account for the observed vapor pressure lowering.

This brief sketch of the various possible explanations is sufficient to indicate the importance of the measurements reported in this paper. It is shown that none of the explanations so far advanced can account for the behavior of this system.

It is impossible, due to lack of space, to present a complete discus-

sion of the author's views as to the mechanism of this process, but they may be summarized as follows:

1. The total internal surface of the gel is much less than  $6 \times 10^6$  cm.<sup>2</sup>
2. The initial stages of the taking up of water consist in the formation of a monomolecular layer of water over the surface.
3. This monomolecular layer in tending to exhibit a minimum surface, produces a capillary effect that is much greater than that as calculated by the classical Kelvin equation.

In other words, the retention of water by silica gel is brought about by the presence of a monomolecular layer which eventually brings about a filling of the capillary spaces under greatly reduced pressures.

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# THE SPECIFIC SURFACE AREA OF ACTIVATED CARBON AND SILICA

BY F. E. BARTELL AND YING FU

IN the study of adsorption and of contact catalysis, it would be highly desirable to know the thickness of the adsorbed layer. At present this problem can not be studied with the desired degree of accuracy because no reliable method is available for the determination of the specific surface area of the adsorbents which in most cases are porous. Various methods for making this determination have been proposed but none of them is sufficiently accurate. In this paper a method will be described which we believe can be used for the determination of the surface area of almost any adsorbent.

## I. A BRIEF REVIEW OF PREVIOUS WORK

The methods previously used for surface area determination may be divided into four main classes:

1. *Adsorption Method*.—This method was first developed by Paneth and Vorwerk<sup>1</sup> to determine the surface area of lead sulfate. A radioactive indicator was used. The method was later extended by Paneth and Radu<sup>2</sup> and applied to carbon. In general it consists in obtaining the adsorption isotherm of a definite solute. The concentration range is extended until the amount of solute adsorbed appears to be independent of concentration. The horizontal part of the curve is interpreted as representing saturation of the surface, *i.e.*, the entire surface of the adsorbent is assumed to be covered by the adsorbate. Knowing the size of the adsorbed molecules and the thickness of the adsorbed layer, the area of the adsorbent can be easily calculated. In their investigation on the adsorption of dyestuffs on diamond Paneth and Radu found the adsorbed layer to be monomolecular. Assuming this to hold also for the adsorption by carbon they determined the surface area of different carbons by adsorption of dyestuffs, lead nitrate, and acetone. For the

<sup>1</sup> Z. physik. Chem., **101**, 445 (1922).

<sup>2</sup> Ber., **57**, 1221 (1924).

same sample of carbon their values varied within a limit of 400 per cent, the highest values being obtained with acetone. They attributed the high value to the smaller size of the acetone molecules, hence its ability to penetrate into the very fine capillary pores of the carbon which are inaccessible to the large molecules of the dyestuffs. It can be shown thermodynamically that the amount of an adsorbate taken up may be dependent to a large extent upon the curvature of the capillary pores of the adsorbent. It is, therefore, evident that the results obtained with the plane surface of diamond powder can not be applied directly to carbon which has an entirely different surface structure, and it is not justifiable to assume *a priori* that the adsorption layer on carbon is also monomolecular. The same comment may be applied to the work of Bachmann and Brieger<sup>3</sup> who compared the amount of methylene blue adsorbed by a graphite plate of known area with that taken up by carbon (darco) and concluded that the specific surface of their carbon was only 2500 sq. cm. By using aqueous solution of alcohols, Garner, Knight, and McKie<sup>4</sup> gave 66 sq. m. as the specific surface of a sample of carbon. Their method consisted in obtaining adsorption isotherms of alcohols from surface tension data and interpreting the break of the curve as representing the completion of the formation of a monomolecular adsorbed layer. Assuming a definite orientation of the adsorbed molecules the surface area can be calculated if the dimensions of the adsorbates are known. There is no definite proof, however, of the correctness of the assumption that the break of the adsorption isotherm corresponds to the completion of a monomolecular layer. There is also no reason to believe that the adsorbed layer consists of alcohol only, the water molecules being excluded. On the contrary, it has been shown in other papers from this laboratory<sup>5</sup> that in the adsorption from binary liquids the adsorbed layer, on carbon at least, never consists of one species of molecules; the solvent molecules as well as the solute molecules are adsorbed. Further, the dimensions of the molecules in question are not definitely known.

**2. Solubility Method.**—This method, originated by Wolff<sup>6</sup> and extended by Schmidt and Durau<sup>7</sup> is not easy to carry out. It consists in determining the solubility of a substance of known area, glass plates for instance, and that of the powdered form. The area of the powder

<sup>3</sup> Kolloid-Z. (Zeigmondy Festschrift), **36**, 142 (1925).

<sup>4</sup> J. Phys. Chem., **31**, 641 (1927).

<sup>5</sup> Bartell and Sloan: J. Am. Chem. Soc., **51**, 1643 (1929); Bartell and Fu: J. Phys. Chem., in press.

<sup>6</sup> Z. angew. Chem., **35**, 138 (1922).

<sup>7</sup> Z. physik. Chem., **108**, 128 (1924).

is calculated from the solubility data by the following equation:

$$\frac{a}{o} = \frac{b}{x},$$

$a$  representing the amount dissolved from the plate of area  $o$ , and  $b$  representing the amount dissolved from the powder of area  $x$ . Whether this method can be applied to all sparingly soluble solids is questionable. In fact, Schmidt and Durau have found that this method can be applied only to certain kinds of glass and is not applicable to other kinds. Besides the difficulty of obtaining the solids in a definite form and with definite area, which is necessary for this method, it is also not known whether it can be applied to solids with fine capillaries such as are found in silica gel. Another serious drawback of this method is that it can not be applied to the most important adsorbent, carbon, because of the lack of a solvent.

3. *Vapor Pressure Method*.—From the relationships between the vapor pressure and the surface curvature in the capillaries, Lowry and Hulett<sup>8</sup> estimated the specific surface of four samples of carbon from the capillary equation as modified by Anderson<sup>9</sup>

$$r = \frac{2Sd_2.4343}{d_1p_0 \log \left( \frac{p_0}{p} \right)},$$

where  $r$  is the radius of the capillaries;  $S$  the surface tension of the liquid;  $d_1$  its density;  $d_2$  the density of the vapor at that temperature;  $p_0$  and  $p$  the vapor pressure of the liquid in bulk and in the capillaries respectively; and 0.4343 the conversion factor of logarithms. Their values for the surface area of four samples of carbon investigated are 100, 230, 300, and 440 square meters. As this equation was derived for ordinary capillaries, it is doubtful whether it can be applied to the micropores of carbon or gel, which are practically of molecular dimensions. Moreover, neither the distribution nor the shape of the capillaries is known. This method therefore can at best serve only as an approximation.

4. *Microscopic Method*.—This method has been used by Parks<sup>10</sup> and Briggs.<sup>11</sup> It consists in measuring microscopically the size of particles.

<sup>8</sup> J. Am. Chem. Soc., **42**, 1393 (1920).

<sup>9</sup> Z. physik. Chem., **88**, 191 (1914).

<sup>10</sup> Phil. Mag., **4**, 240 (1902).

<sup>11</sup> J. Phys. Chem., **9**, 617 (1905).

The surface area can be calculated by assuming that the powder has a definite shape and that its density is not affected by the fine subdivision. These assumptions are evidently not justifiable. Further, the method can not be applied to substances with fine capillary pores such as are possessed by most adsorbents.

In summarizing, we may state that the adsorption method involves assumptions concerning which we have no definite proof; the solubility method is not of general application; the vapor pressure method is likewise limited in application; the microscopic method can at best be used with but few adsorbents.

Owing to our present limited knowledge concerning the thickness of the adsorbed layer, we are not justified in basing a method solely upon the assumption that we are dealing with a monomolecular layer. Accordingly it has seemed highly desirable to develop for the determination of the specific surface area of an adsorbent a method which is free from any assumption regarding the nature or thickness of the adsorbed layer.

## II. THEORY OF DETERMINATIONS

It is well known that heat is evolved when an inert solid is wetted by a liquid. Many theories have been advanced to explain this phenomenon, but none of them seems to be entirely satisfactory. No attempt will be made to discuss the various theories at this point. An attempt will be made to derive an equation for the evaluation of surface area of adsorbents based upon the principle of heat of wetting.

No matter what the mechanism of the heat evolution may be, the heat liberated represents the decrease of total surface energy. If we can evaluate the total surface energy per unit area of the adsorbent, we can calculate the total surface area of that adsorbent. When the surface area of a solid or of a liquid is increased by an amount  $da$  at constant temperature and pressure, the free energy of the system,  $F$ , is increased by  $Sda$ , where  $S$  is the surface tension or free surface energy per unit surface of the solid or liquid. Representing the increase of free energy by  $dF$ , we have

$$dF = Sda$$

$$S = \frac{dF}{da}$$

From this we have

$$\frac{dS}{dT} = \frac{d\left(\frac{dF}{da}\right)}{dT} = \frac{d\left(\frac{dF}{dT}\right)}{da}$$

As  $\frac{dF}{dT}$  is equal to  $-S^\circ$ , the entropy of the surface, it follows

$$\frac{dS}{dT} = \frac{-dS^\circ}{da}$$

Since

$$-S^\circ = \frac{(F - H)}{T}$$

$H$  being the heat content, we have at constant temperature and pressure

$$\begin{aligned}\frac{dS}{dT} &= \frac{-dS^\circ}{da} = \left( \frac{dF}{da} - \frac{dH}{da} \right) / T \\ &= \left( S - \frac{dH}{da} \right) / T\end{aligned}$$

and

$$dH = \left( S - T \frac{dS}{dT} \right) da = dq'$$

$dq'$  being the heat required to increase the surface area by  $da$  at constant temperature and pressure. When a solid is immersed in the liquid, the solid-air interface disappears, therefore,

$$\begin{aligned}\int dq' &= \left( S_s - T \frac{dS_s}{dT} \right) \int_a^0 da \\ q' &= -a \left( S_s - T \frac{dS_s}{dT} \right),\end{aligned}$$

$S_s$  being the surface tension of the solid. The right-hand member of last equation has been shown by Lord Kelvin to be the total surface energy of the solid. After the immersion we have in place of the solid-air surface a solid-liquid interface of the same area with an interfacial tension  $S_i$ . In forming this interface we have to supply an amount of energy  $q''$ , which is equal to

$$\left( S_i - T \frac{dS_i}{dT} \right) \int^a da = a \left( S_i - T \frac{dS_i}{dT} \right),$$

the right-hand member being the total energy of the interface  $a$ . The total heat supplied is equal to the sum of  $q'$  and  $q''$ .

$$Q = q' + q'' = -a (S_s - S_i) + aT \left( \frac{dS_s}{dT} - \frac{dS_i}{dT} \right)$$

Since heat is evolved in the process, we have instead of  $Q$

$$-Q = a (S_s - S_i) - aT \left( \frac{dS_s}{dT} - \frac{dS_i}{dT} \right),$$

where  $-Q$  = the heat of wetting. This equation is the same as that given by Williams<sup>12</sup> and by Harkins and Ewing.<sup>13</sup>

Since  $(S_s - S_i)$  is the adhesion tension the above equation can be written in the following form:

$$-Q = aA - aT\left(\frac{dS_s}{dT} - \frac{dS_i}{dT}\right).$$

Even though  $S_s$  and  $S_i$  can not be determined directly at present, Bartell and Osterhof<sup>14</sup> have succeeded in measuring  $S_s - S_i$  for a number of liquids against carbon and silica. They have also found the relation

$$S_s - S_i = KS,$$

where  $S$  is the surface tension of the liquid in which the solid was immersed, and  $K$  is a constant for the given solid-liquid system. Differentiating the above equation with respect to temperature  $T$ , we have

$$\frac{dS_s}{dT} - \frac{dS_i}{dT} = K \frac{dS}{dT}.$$

Substituting this in the equation for the heat of wetting we have

$$-Q = a\left(A - K \frac{dS}{dT} \times T\right),$$

and the surface area  $a$  is given by the following equation:

$$a = \frac{-Q}{A - KT \frac{dS}{dT}}$$

As  $-Q$ ,  $A$ ,  $K$ , and  $\frac{dS}{dT}$  can be determined experimentally, the area  $a$  can be evaluated.

In deriving the above equation it was assumed that  $K$  is independent of temperature. At present there are no experimental results to prove or disprove this point, but the assumption appears to be justified and the error introduced by this assumption, if any, must be very small.

This method of determining surface area does not depend on the measurement of adsorption from solution; it is therefore free from those uncertainties which arise from the use of doubtful assumptions concerning

<sup>12</sup> Proc. Roy. Soc. Edinburgh, **38**, 24 (1918).

<sup>13</sup> J. Am. Chem. Soc., **43**, 1787 (1921).

<sup>14</sup> Z. physik. Chem., Cohen-Festband, 715 (1927); Colloid Symposium Monograph (1927).

the shape and dimension of the adsorbed molecules, and the unknown thickness of the adsorbed layer, which assumptions are unavoidable in the adsorption method as used at present. This method can be applied to those solids for which there is no solvent, because the method does not depend on solubility determinations. It is also evident that this method is more reliable than the vapor pressure or the microscopic methods.

### III. EXPERIMENTAL WORK

**Apparatus.**—The calorimeter used in this work consisted of a Dewar flask similar to that used by Patrick and Grimm.<sup>16</sup> Minor modifications were made in the apparatus. The flask had a ground glass cover. Both the Beckmann thermometer and the heater were cemented through the cover with DeKhotinsky cement. The stirrer was sealed with mercury. When the bulb with the solid was finally set in position the flask was strictly gas-tight.

**Materials: Carbon.**—This was prepared from Merck's pure cane sugar by charring in a platinum dish. After it was charred the carbon was ground in an agate mortar to a fine powder and was heated to 1200° C. for twelve hours in the absence of air. This carbon was then heated in an alundum thimble at the same temperature for six hours with a limited supply of air. It was then cooled in a desiccator and stored in a weighing bottle for use.

**Silica.**—Gels were first prepared by the method of Patrick and McGavack<sup>17</sup> and of Holmes and Anderson,<sup>18</sup> but the results were not entirely satisfactory. The following method was finally adopted. A good grade of water glass was diluted to three times its original volume and then neutralized with 1 : 1 HCl. Before the silicic acid thus formed had set to a jelly a saturated solution of  $\text{Ni}(\text{NO}_3)_2$  was added with rapid stirring. After the silicic acid had set into a beautiful clear green gel, it was dried at 90° C. for four days. The gel, now black, was poured into cold water. The main portion of the Ni salt was easily removed by washing with water and the last trace finally removed with HCl. The white gel was transferred into a quartz dish and was heated in an electric

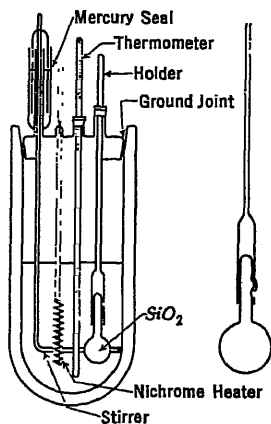


FIG. 1a and 1b.

<sup>16</sup> J. Am. Chem. Soc., **43**, 2144 (1920).

<sup>17</sup> J. Am. Chem. Soc., **42**, 946 (1920).

<sup>18</sup> J. Ind. Eng. Chem., **17**, 280 (1925).

oven at  $260^{\circ}$ . After five hours the gel was taken from the oven and poured immediately into cold conductivity water. The major portion of HCl was removed by the first washing. This drying and washing was repeated seven or eight times. The gel was finally dried at the same temperature ( $260^{\circ}\text{C.}$ ). The washing water had a pH of 6.8 as determined by Dawson's method, after the second treatment. The silica gel so obtained was white and transparent, and could be ground into powder very easily. It contained 4 per cent water. The water was finally removed by heating the gel with a blast lamp. On treating with HF it left less than 0.005 per cent residue.

*Water.*—Conductivity water used throughout.

*Ethyl Alcohol.*—Absolute alcohol was treated with lime and refluxed four hours, then distilled. The distillate was treated with metallic sodium and redistilled, first and last portion being rejected.

*Iso-amyl Alcohol.*—Redistilled alcohol was treated with  $\text{K}_2\text{CO}_3$  and then distilled.

*Benzene.*—Thiophene free benzene was frozen out twice, dried with metallic sodium and then distilled.

*Carbon Tetrachloride.*—Commercial  $\text{CCl}_4$  was treated with concentrated sulfuric acid, washed thoroughly with water and NaOH, dried with  $\text{P}_2\text{O}_5$  and fractionated.

*Chloroform.*—Same as  $\text{CCl}_4$ .

*Nitrobenzene.*—Commercial mononitrobenzene was treated with NaOH, washed with water, dried with  $\text{CaCl}_2$ , and fractionated.

*Carbon Disulfide.*—Commercial  $\text{CS}_2$  was treated with Hg and  $\text{HgCl}_2$ , refluxed, washed with water, dried with  $\text{P}_2\text{O}_5$ , and fractionated.

*Ethyl Carbonate.*—Pure ethyl carbonate from Eastman Kodak Co. was redistilled.

*Acetone.*—This was purified by the NaI method of Shipsey and Werner.

**Method.**—The solid was sealed in a thin-walled glass bulb, the latter was then sealed on the glass holder. (Fig. 1b.) After the bulb was introduced, the whole apparatus was placed in the felt jacket. The liquid was constantly stirred until the temperature remained constant for at least half an hour. The bulb was then broken by pushing it gently against the wall of the calorimeter, and the change in temperature was read from the Beckmann thermometer. In all cases the temperature change indicating complete wetting reached its maximum within two minutes. The heat capacity of the whole apparatus was determined after the temperature had returned to its original value by passing a definite electric current through the heater for a given time; the temperature change was again noted. By using this procedure it was not



to know the heat capacity of the Dewar flask, the thermometer, the stirrer, or the solid, so the error that might be introduced in specific heat determinations was eliminated. In each case the total thermal leakage was corrected by calibration using the method of White.<sup>19</sup> In order to insure no evaporation of the liquid in the interval between the wetting of the solid and the determination of the heat capacity of the apparatus, one determination was prolonged to four hours, and the result was found to be within the limit of total error. It was therefore concluded that the error, if any, due to the evaporation of the liquid during the period of experiment, was negligible. The results obtained on the heat of wetting and surface area for both carbon and silica are given in Tables 1 and 2.

TABLE 1.—HEAT OF WETTING AND SURFACE AREA OF SUGAR CHARCOAL

	$-Q$	$A$	$K$	$dS_i/dT$	$a$
e..	28.57 28.75 28.08 28.85 28.56	81.1	2.87	-.130	$6.2 \times 10^8$ sq. cm.
e..	29.5 29.7 30.6 30.5 30.1	79.83	3.04	-.134	$6.3 \times 10^8$ sq. cm.
e..	30.6 31.0 30.9 31.4 31.2	89.45	2.65	-.161	$6.1 \times 10^8$ sq. cm.
O <sub>2</sub> e..	26.2 26.6 26.4	65.55	2.54	-.122	$6.8 \times 10^8$ sq. cm.
e..	30.75 30.90 31.25 31.00 30.97	86.37	3.3	-.120	$6.3 \times 10^8$ sq. cm.
Average from five determinations.....					$6.3 \times 10^8$ sq. cm.

# SPECIFIC SURFACE AREA OF ACTIVATED CARBON AND SILICA

TABLE 2.—HEAT OF WETTING AND SURFACE AREA OF SILICA

	$-Q$	$A$	$K$	$dS_i/dT$	$a$
	15.90	82.82	1.15	-.1511	$5.0 \times 10^6$ sq. cm.
	15.90				
	15.80				
	15.91				
	16.03				
	15.91	.....	.....	.....	
	12.56	42.43	1.85	-.140	$4.3 \times 10^6$ sq. cm.
	12.50				
	12.73				
	12.66				
	14.22	59.95	2.25	-.113	$4.5 \times 10^6$ sq. cm.
	14.85				
	14.50				
	14.52				
	12.05	63.45	1.48	-.114	$4.5 \times 10^6$ sq. cm.
	12.40				
	12.09				
	12.5				
	12.3				
	10.0	40.7	1.56	-.128	$4.3 \times 10^6$ sq. cm.
	10.0				
	10.0				
ave determinations.....					$4.5 \times 10^6$ sq. cm.

## IV. DISCUSSION

From the tables it is seen that specific surface areas calculated from heat of wetting data with different liquids are consistent. For the greatest deviation from the mean is less than 7 per cent, that of silica is about 10 per cent. This compares favorably with Radu's results which have been considered the most accurate.

Values for specific surface of silica obtained from heat of wetting are higher than that obtained with the other liquids. This is expected since water has the highest adhesion tension of all of the liquids studied against silica; it is difficult for the organic liquids to displace water from a silica surface. When the silica was transferred

to the glass bulb, it undoubtedly took up some moisture from the air, due to the hygroscopic nature of silica. Since the heat of wetting depends on the surface area actually brought into contact with the liquid, smaller values are to be expected in case some of the surface was already occupied by water. The specific area of carbon,  $6.35 \cdot 10^6$  sq. cm., is higher than most values recorded in the literature. Of course, this might be due to different methods of preparation of the samples, but a higher value by this method is to be expected even if identical samples are used. Granting the adsorption layer to be monomolecular, the adsorption method, which is the most accurate of the four mentioned above, would give a lower value as it does not take into consideration the adsorption of the solvent which undoubtedly takes place.

It is obvious that in order to obtain reliable values the liquid used must not undergo any chemical change when it comes into contact with the solid. Hence inert liquids are preferable. This is illustrated by the wetting of carbon by alcohol. As is well known, adsorptive carbon has a great affinity for oxygen. When carbon is wetted by alcohol, a small portion of the liquid may be oxidized by the adsorbed oxygen under the catalytic influence of the solid. Therefore the heat observed will probably be too high. The specific surface of carbon calculated from the amyl alcohol values is higher than that from other liquids. Another factor which contributes to the uncertainty of the values obtained with the alcohols is the difficulty with which their adhesion tensions are determined. The higher alcohols, such as amyl alcohol, are slightly soluble in water. In the determination of adhesion tension of carbon, water is used with the organic liquid in the displacement cell. The interfacial tension of water against alcohol is a function of the solubility of alcohol which in turn is a function of pressure. Since there is a volume decrease when alcohol is dissolved in water, it can be shown from the second law of thermodynamics that the solubility of alcohol in water is increased under the high adsorption pressure such as exists in fine capillaries. Since we have no quantitative data on the solubility of alcohols under these conditions, considerable uncertainty is introduced regarding the interfacial tension values used in the calculation of adhesion tensions.

The heats of wetting of silica determined for ethyl alcohol and for the acetone are higher than that for water. This agrees with the results of Patrick and Grimm who also observed this relationship with ethyl alcohol, water, and silica gel. They explained this higher heat of wetting by assuming the formation of a water-alcohol interface in the capillaries and by further assuming that the interfacial tension has a positive temperature coefficient. This explanation does not seem very rational.

Even though it were true, it can not be applied to the experiments discussed herein as there was no appreciable amount of water on our silica. This high value can, however, be explained from the surface energy relationships. Since no data exist as to the adhesion tension values of these two liquids against silica, the change in total energy must be evaluated indirectly. This can be done as follows:

From the equation

$$-Q = a \left( A - KT \frac{dS}{dT} \right)$$

the following expression is obtained:

$$-Q = a \left( A - \frac{A}{S} T \frac{dS}{dT} \right), \text{ because } K = \frac{A}{S}$$

From this we have

$$-QS = aA \left( S - \frac{TdS}{dT} \right)$$

and

$$A = \frac{-QS}{a \left( S - \frac{TdS}{dT} \right)}.$$

Using  $4.5 \times 10^6$  sq. cm. as the specific area of silica, we obtained

$$A = \frac{75 \text{ dynes}}{\text{cm.}}$$

$$K = 3.5$$

for alcohol, and

$$A = \frac{62 \text{ dynes}}{\text{cm.}}$$

$$K = 2.77$$

for acetone.

With a gel containing 4 per cent water the heat of wetting and specific surface area value were determined with four liquids—water, ethyl alcohol, acetone, and benzene. The results collected are in Table 3.

The agreement of the values obtained with organic liquids is excellent while water gave a slightly higher value (this was to be expected because the solid may be considered to be already somewhat wetted with water). In the calculations of the specific area of the hydrated silica it was assumed that the water was distributed uniformly throughout the gel and did not exist as a water layer around the silica particles, as Patrick

and Grimm have assumed. In other words, the silica surface was assumed to be a composite surface of both silica and water molecules but with silica predominating. If the water present were to form a complete layer on the silica surface, the following equation should be used for calculating the specific surface area:

$$a = \frac{-Q \times 4.182 \times 10^7}{E_{\text{H}_2\text{O}} - E_i},$$

where  $E_{\text{H}_2\text{O}}$  is the total surface energy of water and  $E_i$  is that of interface, water-organic liquid.

TABLE 3.—HEAT OF WETTING OF SILICA

Anhydrous silica-ethyl alcohol -Q		Silica-acetone -Q	
16.64 16.72 16.60 16.65 16.60 Average 16.64		16.80 16.95 16.80 16.76  Average 16.83	
Hydrated Silica-alcohol		Hydrated Silica-acetone	
-Q	a	-Q	a
27.0 26.8 27.0 27.1 27.4 Average 26.9	$7.0 \times 10^6$	27.2 26.9 26.8 26.7 Average 26.9	$7.2 \times 10^6$
Hydrated Silica-water		Hydrated Silica-benzene	
-Q	a	-Q	a
24.20 24.15 24.22 24.50 Average 24.31	$7.5 \times 10^6$	21.5 21.8 21.2 Average 21.5	$7.3 \times 10^6$

This type of calculation was made by Patrick and Grimm. As we have no available values of interfacial tensions of water-alcohol or water-acetone, we can only compare the values obtained from water and benzene. By this treatment we obtain, then, for the specific surface of the silica used

$$8.68 \times 10^6 \text{ sq. cm. from water value}$$

$$13.0 \times 10^6 \text{ sq. cm. from benzene value}$$

It has often been considered that the higher the heat of wetting the greater the adsorption. If a liquid with a high heat of wetting is used as a solvent, then less adsorption of the solute will occur from that solution.<sup>20</sup> From the present investigation it is evident that this generalization is not correct. Whether a liquid will be strongly or slightly adsorbed depends on its adhesion tension against the solid. Adhesion tension is the measure of the decrease of free surface energy; and according to Gibbs' theorem of adsorption, that component which lowers the surface tension, that is, the free surface energy, will tend to be positively adsorbed. As shown from the data in this paper, a liquid with low adhesion tension may have a higher heat of wetting than the one with a greater adhesion tension. This is because heat of wetting is the measure of the decrease of total surface energy and not the free surface energy; the latter determines the degree of adsorption of the liquid by the solid. If a liquid with a high adhesion tension be used as solvent, the adsorbent will take up considerable amounts of the solvent; hence the adsorption of the solute will be low. If a liquid with high heat of wetting instead of high adhesion tension be used as solvent, a corresponding relationship may not result. Thus it can be shown silica adsorbs better from acetone than from water solutions and carbon adsorbs better from nitrobenzene than from alphas-bromonaphthalene even though the former two gave the higher heat of wetting.

#### SUMMARY

A brief review of the available methods for the determination of specific surface area of adsorbents has been given and their limitations discussed.

A new method based on heat of wetting and adhesion tension values has been developed for the determination of specific area of adsorbents and applied to carbon and silica. Independent determina-

<sup>20</sup> Berl and Wachendorff: *Kolloid-Z. (Zsigmondy Festschrift)*, **36**, 36 (1925).

tions of the surface area of these solids were made using a number of different liquids. The results obtained checked satisfactorily in each case.

Adhesion tensions of ethyl alcohol and acetone against silica were calculated from heat of wetting data.

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## COMPOUND FORMATION WITH A VOLATILE BASE OR ACID<sup>1</sup>

BY WILDER D. BANCROFT, C. E. BARNETT, AND B. C. BELDEN

It is an easy matter to tell whether an acid, a base, or a dye is adsorbed by silk, wool, cotton, rayon, or paper. We can treat the fibers with solutions of varying concentrations and see whether the amount taken up plotted against the amount left in solution gives a smooth curve, indicating adsorption, or a curve with a flat in it indicating the coexistence of two solid phases. From the form of the curve we can tell whether the second phase is a compound, and, if so, what its composition is. We cannot do this with proteins, such as gelatin and casein, because they are peptized and there is no way at present of analyzing the two or more phases with any degree of accuracy. Since one may postulate ammonium gelatinate or gelatin hydrochloride with any desired degree of hydrolysis and dissociation, and any desired properties, it becomes practically impossible to devise an experiment which will be conclusive to a prejudiced opponent—and all opponents are prejudiced.

It seemed desirable therefore to eliminate the solution phase and to treat the powdered protein with ammonia or hydrogen chloride gas, noting the amounts taken up and the corresponding pressures.<sup>2</sup> If there is an ammonium caseinate or an ammonium gelatinate, the pressure must remain constant until all the casein or gelatin has been converted into the ammonium compound. If ammonia is adsorbed by the protein, there will be a smooth curve characteristic of adsorption. At the Detroit meeting of the American Chemical Society, a report was made before the Division of Physical and Inorganic Chemistry on some preliminary experiments by Mr. Tsunajima, which showed that ammonia was adsorbed by casein and did not form any definite compound with it. Many of the people in the audience were so unfamiliar with the

<sup>1</sup> This work is part of the program now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

<sup>2</sup> Cf. Lescœur: *Ann. chim. phys.*, (6) **19**, 35, 533 (1890); Meyer and Rötgers: *Z. anorg. Chem.*, **57**, 104 (1908); Browne and Houlehan: *J. Am. Chem. Soc.*, **35**, 649 (1913).

phase rule that they did not appreciate the significance or the conclusiveness of the evidence. When they learned that we had not tested the method on known acids and on simple amino acids, they expressed the opinion that the same type of curve would be obtained regardless of whether there was adsorption or compound formation. While this is, of course, foolishness, the simplest way to meet it is to furnish the data, and we are doing this.

A weighed amount of powdered base or acid is placed in a vessel of known volume, a known amount of hydrogen chloride or ammonia is run in, and the difference between the observed and the calculated pressures is a measure of the amount of gas adsorbed. Since the temperature is kept constant, there can be only one pressure when we have two solids and vapor. A flat in the pressure curve followed by a theoretically perpendicular branch means a compound having the composition represented by the reading on the abscissas of the point at which the nearly vertical branch of the curve starts. At ordinary temperatures the dissociation pressures of the compounds which we have studied have been less than 5 mm.

Under these circumstances, it is quite immaterial whether our substance is pure or not, provided all we wish to determine is whether we are forming definite or indefinite chemical compounds, meaning thereby compounds described by the laws of definite and multiple proportions or adsorption complexes. Suppose that what we called gelatin was really a mixture of ten different acids—or more if one wants more. There would then be ten—or more—flats, with a nearly perpendicular rise after the last one. If the ten or more flats are bunched within 5 mm. they will not mislead anybody into thinking that the steps constitute a curved ramp.

We have worked at ordinary temperatures because that is the easiest thing to do, and because we get the most striking results under these conditions. If anybody wants to have the flat come at 100 mm. or at 500 mm. instead of at less than 5 mm., all he has to do is to raise the temperature. The only limit is the temperature at which the substance or the ammonia begins decomposing. If one works at different temperatures, one can get data from which to calculate heats of dissociation, free energy, etc. One could also determine values for *o*-, *m*-, and *p*-amino benzoic acids if he wished, and could compare these results with those calculated from conductance measurements. We have not done that because it did not seem especially interesting just now.

More interesting is the fact that the presence or absence of water makes no difference in the general form of the curve. If we add ammonia to a saturated solution of oxalic acid, for instance, there will be no flat

until the solution is saturated both with respect to oxalic acid and with respect to an ammonium oxalate. The pressure measured along the flat will be the dissociation pressure of the acid ammonium oxalate plus the partial pressure of the water in equilibrium with the saturated solution; but that should not confuse anybody. The essential thing is that there is a flat in the curve. The ammonia composition at which the flat ends is no longer the composition of the acid ammonium oxalate, but the amount of ammonia in the compound and in the solution at which there ceases to be any oxalic acid as solid phase. This will vary with the relative amount of water and oxalic acid; will not affect the conclusions to be drawn from the diagram. This is very important because the

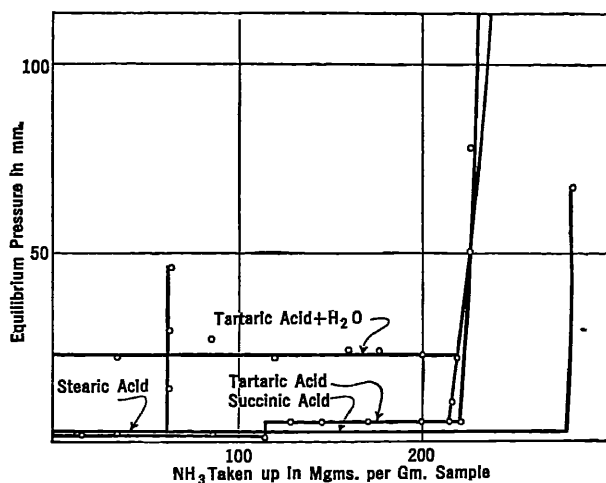


FIG. 1.

believers in ammonium gelatin ate would unquestionably have raised the point, which may be well taken, that drying gelatin completely changes it. The presence in gelatin of varying amounts of water does not interfere in any way with the proof that ammonium gelatin ate is not formed at ordinary temperatures.

In Fig. 1 are shown the curves for stearic acid, succinic acid, and tartaric acid with ammonia, the abscissas being milligrams of ammonia per gram of acid because that brings the rises at different places. All the curves consist of a flat and a nearly vertical rise, the characteristic curve for a compound. With tartaric acid one can detect two compounds, but not with succinic acid. In the curve entitled tartaric acid and water, the partial pressure of the water vapor (there was no liquid water) is superposed on the flat for tartaric acid. The detection of the

compound is practically as sharp as with the dry acid and it takes less time to reach equilibrium.

When we plot as abscissas mols of ammonia taken up per mol of acid, as in Fig. 2, the two dibasic acids, tartaric and succinic, come practically together, and we see that stearic acid is a monobasic acid. The dissociation pressures are so low that measurements were made at room temperatures without using a thermostat. At higher temperatures, it is probable that one could detect the difference between the

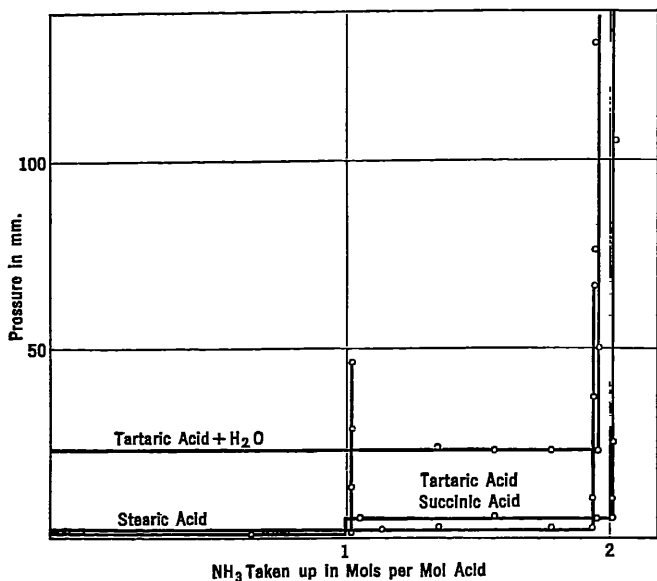


FIG. 2.

first and second mols of ammonia to succinic acid; but that was not part of our problem.

In Fig. 3 we have the data for hydrogen chloride and for hydrogen sulphide with aniline. Aniline is a liquid with a negligible vapor pressure under the conditions of the experiment. As soon as aniline hydrochloride crystallizes, we have three phases, solid, liquid, and vapor. Consequently the pressure remains constant, so long as the temperature does. With hydrogen chloride we get the characteristic curve for a solid compound with aniline. The break comes at about 37 mg. HCl per 100 mg. aniline as against about 39 mg. for aniline hydrochloride. Traces of impurity in the aniline would account for this slight discrepancy. With hydrogen sulphide there is no evidence of the formation of any solid aniline hydrosulphide. Since the adsorption of hydrogen sulphide

follows Henry's law so accurately up to pressures of over 1200 mm., it is probable that there is practically no formation of a definite chemical compound in solution.

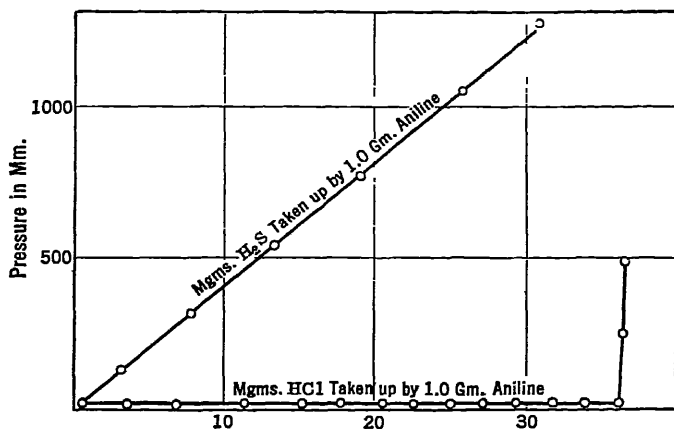


FIG. 3.

We next tried the simplest of the amino acids, amino-acetic acid. To our surprise and rather to our dismay, it took up practically no

ammonia at all. We felt better after we had consulted the literature and had found that amino-acetic acid crystallizes pure from a concentrated aqueous solution of ammonia. If one takes a stronger amino acid, one can get compounds. In Fig. 4 are shown curves for amino-acetic acid, amino-benzoic acid, a mixture of amino-benzoic acid and amino-sulfonic acid, and the crude and purified glutamic acid as furnished by the Eastman

Kodak Company. All the acids except amino-acetic acid form

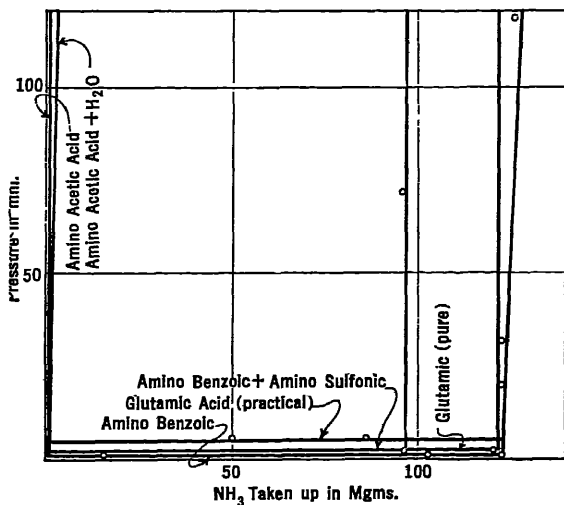


FIG. 4.

definite chemical compounds with ammonia. By working at different temperatures with different amino-benzoic acids or different substituted

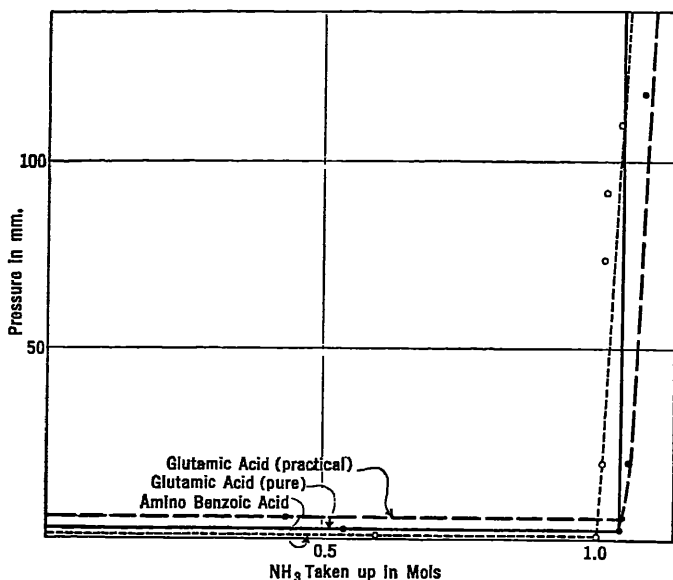


FIG. 5.

benzoic acids, it would be easy to get plenty of data in regard to the free energy of substituted ammonium benzoates. The presence of amino-

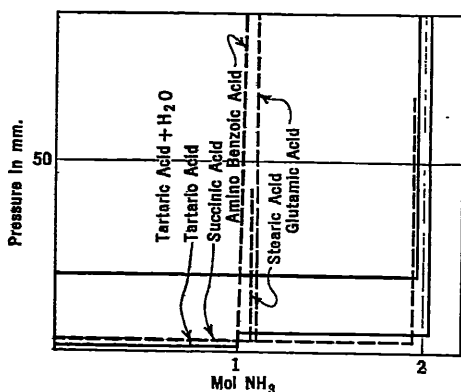


FIG. 6.

sulfonic acid as an added impurity in the amino-benzoic acid merely shifts the curve to the left, because the molecular weight of amino-sulfonic acid is less than that of amino-benzoic acid. The difference between the pure and the "practical" glutamic acid is negligible so far as the principle goes. As a matter of fact, the crude glutamic acid is easily purified by shaking a solution

with charcoal and crystallizing. The difference in price of the two products seems excessive.

It is not easy to titrate glutamic acid even with a strong base, and yet we get a sharp end-point by the ammonia method. One wonders

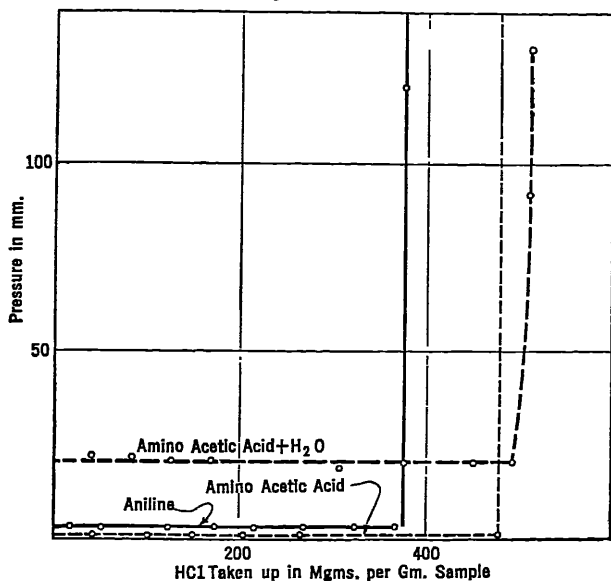


FIG. 7.

whether this might not be a good method of determining the amount of ionizable hydrogen in weak acids. Something of this sort has already been done by Dr. Levene of the Rockefeller Institute.

In Fig. 5 are shown the data for amino-benzoic acid and for the two samples of glutamic acid when the abscissas are mols of ammonia taken up per mol of solid acid. While the curves do not coincide absolutely, they come pretty close together and they show distinctly that glutamic acid is functioning as a monobasic acid

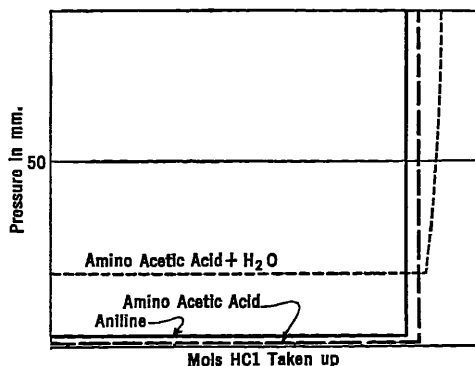


FIG. 8.

under these conditions. In Fig. 6 these same data are shown, together with the data for tartaric, succinic, and stearic acids from Fig. 2. This should dispel any idea that there is anything mysterious or abnormal about the amino acids.

While amino-acetic acid is not a strong enough acid to form a compound with ammonia, it forms a definite compound with hydrogen

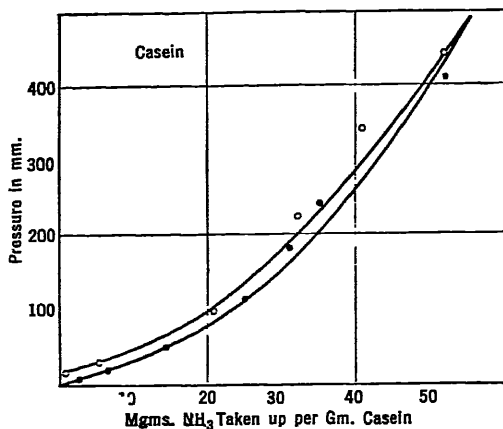


FIG. 9.

chloride, as may be seen from Fig. 7, where are given the data for amino-acetic acid and for aniline. In the curve labeled "amino-acetic acid and water," the flat portion of the curve is raised because of the partial pressure of the water vapor. The difference in the upright portion of the curve may be due to some adsorption of water vapor causing a slight adsorption of ammonia.

In Fig. 8 are the same data plotted with mols hydrogen chloride per mol solid base along the abscissas. There is no question but that amino-acetic acid is functioning as a univalent base.

In Fig. 9 are the data for purified casein and ammonia. This is an entirely different type of curve and shows no sign of the formation of a compound. As is so generally the case with adsorption, there is a certain amount of hysteresis, the curve on addition of ammonia (circles) differing a little from the curve on removal of ammonia (dots). This is the same type of curve that was obtained by Mr. Tsunajima. Casein will adsorb at least 55 mg. ammonia per gram of casein at 500 mm. pressure without showing any sign of compound formation.

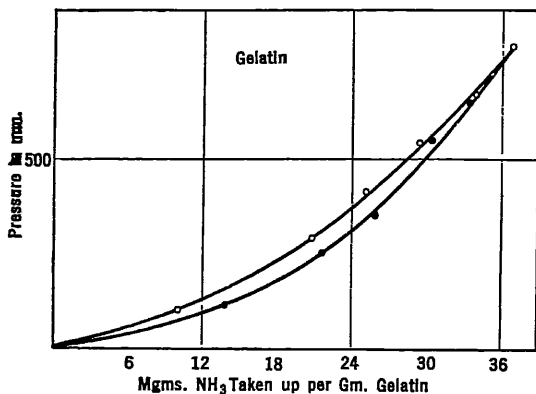


FIG. 10.

In Fig. 10 are given the data for Eastman Kodak ash-free gelatin and ammonia. This is obviously an adsorption curve with a certain



amount of hysteresis. If one takes 1090 as the equivalent weight of gelatin, which is a popular figure at present, this corresponds to between 15 and 16 mg. of ammonia per gram of gelatin. Actually we have 36 mg. taken up without any sign of compound formation. It was suggested at Detroit that gelatin might consist of a hundred or a thousand amino acids with such dissociation pressures that the curve was a succession of small steps and not really a smooth curve. As a flight of fancy, this is possible; but we have not yet found any amino acids which could be mixed to give anything approaching such a curve. That any such grouping of hypothetical acids should occur both with gelatin and with casein seems hopelessly improbable, and the burden of proof is on whoever advances such a guess. We propose to hydrolyze gelatin and to see what the dried product does with ammonia and with hydrogen chloride; but it was impossible to get these data in time for this meeting.

### CONCLUSIONS

The general conclusions to be drawn from this paper are:

1. The pressure-concentration curves for ammonia or hydrogen chloride with solid acids or bases show clearly whether a definite chemical compound is or is not formed.

2. Presence of moderate amounts of water or other impurities displaces the curve but does not change the type.

3. With tartaric acid measurably different dissociation pressures are obtained for the two ammonium salts; but this is not the case for succinic acid. At higher temperatures it would probably be possible to differentiate the two ammonium salts of succinic acid.

4. Owing to the slight solubility of aniline hydrochloride in aniline, it is possible to apply the method even though aniline is a liquid at room temperature.

5. Hydrogen sulphide and aniline follow Henry's law surprisingly well at least up to pressures of 1200 mm. There is no evidence of any aniline hydrosulphide being formed.

6. Amino-acetic acid takes up practically no ammonia gas. This is in line with the known fact that the free acid will crystallize from a concentrated solution of ammonia in water.

7. Amino-acetic acid forms a definite chemical compound with hydrogen chloride.

8. Amino-benzoic acid and glutamic acid form definite chemical compounds with hydrogen chloride, the glutamic acid behaving as a monobasic acid.

9. As first suggested by Dr. Levene, it is quite possible that one could use the treatment with ammonia or hydrogen chloride as a means of determining the approximate purity of a weak acid or a weak base when titration methods prove unsatisfactory.

10. Casein and gelatin adsorb ammonia readily with no evidence of the formation of any definite chemical compound. There is no reason to believe that either the gelatin or the casein—much less both—is made up of innumerable acids of such nature as to give a step-wise curve which is indistinguishable experimentally from a smooth curve.

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# NATURE OF INTERACTION BETWEEN HYDROUS OXIDES AND MORDANT DYES<sup>1</sup>

BY OTTO REINMUTH AND NEIL E. GORDON

SOME years ago, in the course of a study of the effect of hydrogen-ion concentration on the so-called adsorption of dyes by hydrous oxide gels, one of us and Marker<sup>2</sup> remarked certain phenomena which were interpreted at that time as indicative of compound formation. The behavior of Orange II, applied to hydrous oxide gels of aluminum and iron at varying hydrogen-ion concentrations, seemed to present particularly convincing evidence of chemical interaction between the dye and the adsorbent gel. Briefly summarized, the relevant observations made at that time were as follows:

Firstly, curves obtained by plotting *pH* values against milligrams of dye removed from solution per gram of gel, showed marked and rather sharp alterations in their slopes at low *pH* values. Secondly, it was found that solutions containing varying concentrations of dye,<sup>3</sup> but adjusted to the same *pH* values,<sup>4</sup> arrived at practically identical dye concentrations when allowed to come to equilibrium with alumina and iron gels. Thirdly, analyses of samples of the supposed dye-metal compounds agreed with calculated values for those compounds within the limits of experimental error. At that time it was also noted that aluminum or ferric salts, either in solution or in the solid state, produced precipitates when added to solutions of Orange II. These precipitates were believed to be the slightly soluble dye salts of aluminum and ferric iron, respectively, although no analyses were made.

Some time later Weiser and Porter<sup>5</sup> questioned these conclusions and

<sup>1</sup> This paper is an abstract of a portion of a thesis submitted by Otto Reinmuth to the faculty of chemistry of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Marker and Gordon: *Ind. Eng. Chem.*, **16**, 1186 (1924).

<sup>3</sup> Concentrations of 0.5 per cent, 0.75 per cent, and 1.16 per cent were employed.

<sup>4</sup> Unfortunately the actual *pH* value has not been recorded but it was somewhat below 3.0.

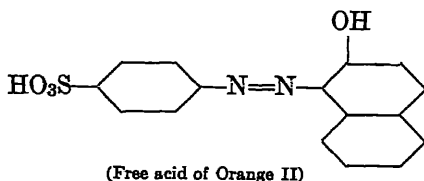
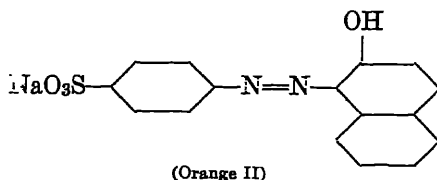
<sup>5</sup> *J. Phys. Chem.*, **31**, 1704 (1927); see also Colloid Symposium Monograph, **5**, 369 (1928); and Weiser: "A Survey of American Chemistry," **3**, 43, 44 (1928).

criticized in detail certain portions of the experimental work upon which they were based, at the same time advancing other explanations to account for the phenomena observed. They furthermore recorded certain experimental observations of their own which were advanced as tending to disprove the theory of compound formation. We shall discuss those criticisms and observations in their appropriate connections in the present paper. Suffice it to say at this point that, while the remarks of Weiser and Porter cast doubt upon the validity of our original conclusions, they involved certain obviously erroneous assumptions and failed in several particulars to account satisfactorily for all of the phenomena of which we had knowledge. On the whole it seemed highly desirable to re-examine the entire matter thoroughly.

### I. INTERACTION OF ORANGE II AND $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

One of the strongest indications of compound formation previously noted had been the constancy and equivalency of chemical composition of the product obtained. We decided, therefore, to make a number of preparations under varying conditions in order to eliminate the possibility of hitting upon some one unfortunate coincidence of conditions which might lead to the formation of a heterogeneous product in which the dye radical and the metal ion might accidentally appear in equivalent quantities.

It may be well to preface an account of the procedures followed with the statement that Orange II is the sodium salt of 2-hydroxy-1-phenylazonaphthalin-1<sup>4</sup>-sulfonic acid, to use the system of numbering employed by Richter. The respective structural formulæ are as follows:



For the purpose of this investigation Orange II may be regarded merely as the sodium salt of a substituted sulfonic acid. As a matter of con-

venience we shall occasionally refer to the dye radical or ion as X, to the dye itself as NaX, and to the free acid as HX.

On this basis one might anticipate the possibility of a metathetic reaction between aluminum chloride and the dye, according to the equation:



with the equilibrium shifted almost completely to the right if the product,  $\text{AlX}_3$ , proved to be but slightly soluble.

We investigated this hypothetical reaction by preparing and analyzing three products. The first was obtained as follows: About <sup>6</sup> 13.5 gm. of Orange II<sup>7</sup> ( $\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}_25\text{Na} \cdot 5\text{H}_2\text{O}$ ) was dissolved in approximately 1 liter of distilled water and filtered. About 2.5 gm. of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in approximately 100 cc. of distilled water and filtered. The solutions were combined in the cold with stirring. The heavy, orange-yellow, apparently amorphous precipitate which remained suspended throughout the liquid was filtered off with the aid of suction, a perfectly clear filtrate being obtained. The filter cake was washed with 200 to 300 cc. of distilled water. Preliminary experiments showed washing to be necessary, for the precipitate occludes and carries down some unchanged Orange II, as evidenced by the fact that sodium can be detected in the ignition residues. Since the product precipitated is pulverulent rather than gelatinous, the necessary washing is accomplished quite readily. The completion is indicated when the highly colored filtrate containing the excess of Orange II gives place to a faintly colored filtrate containing some of the product in solution and some dye acid arising from hydrolysis. The amount of water used in rinsing was so chosen that a small quantity (about 50 cc.) of faintly colored filtrate passed from each sample.

The product was well drained and partially dried by suction and then allowed to air-dry for several days at room temperature. The cake which had then deepened in color to a reddish orange and had become hard and brittle was ground in a hand mortar and samples were taken for analysis.

The dye radical was determined by a slight modification of the  $\text{TiCl}_3$  method outlined by Knecht and Hibbert<sup>8</sup> for Orange II. The deviation consisted in the fact that individual samples of 0.1 gm. were analyzed instead of aliquot parts from a solution of one sample.

<sup>6</sup> These quantities were weighed on a rough laboratory balance.

<sup>7</sup> The dye used was concentrated Orange II furnished by the du Pont Company through the courtesy of Mr. E. K. Bolton.

<sup>8</sup> "New Reduction Methods in Volumetric Analysis," Longmans, Green & Co., New York City, 76 (1918).

Aluminum was determined by igniting 0.5-gm. samples of the product in covered platinum crucibles and blasting to constant weight.

Moisture content was determined by drying 0.5-gm. samples to constant weight at 120 to 125° C. in a Freas electric oven. The samples were dried in small glass-stoppered weighing bottles, the stoppers of course being removed while samples were in the oven, but immediately replaced whenever they were withdrawn.

The results of our analyses on this product were as follows:

Per cent H <sub>2</sub> O.....	{ 19.33 19.20 }	Average.....	19.27
Per cent Al.....	{ 2.32 2.35 }	Average.....	2.34
Per cent X.....	{ 78.30 78.42 }	Average.....	78.36
			<hr/> 99.97

Reduced to a dry basis these figures give 2.88 per cent of Al as compared with a calculated value of 2.67 per cent for  $AlX_3$ , and 97.05 per cent of X as compared with the calculated value of 97.33 per cent.

The quantities of dye and  $AlCl_3 \cdot 6H_2O$  used in the preparation of the product just described represent an *equivalent* ratio of 1 : 1. Two other preparations were made and analyzed in the same manner except that *equivalent* ratios of 2 : 1 and 1 : 2, respectively, were used. The actual quantities employed were 27.0 gm. of dye to 2.5 gm. of  $AlCl_3 \cdot 6H_2O$  in the first case, and 13.5 gm. of dye to 5.0 gm. of  $AlCl_3 \cdot 6H_2O$  in the second case. The analyses were as follows:

	2 Dye : $\frac{1}{2}AlCl_3$			1 Dye : $\frac{1}{2}AlCl_3$		
	No. 1	No. 2	Average	No. 1	No. 2	Average
Per cent H <sub>2</sub> O....	19.11	18.95	19.03	17.73	17.73	17.73
Per cent Al.....	2.25	2.24	2.25	2.40	2.39	2.40
Per cent X.....	78.87	78.99	78.93	79.14	79.36	79.25
	100.23	100.18	100.21	99.27	99.48	99.38

The average analyses for all three products, reduced to a dry basis, are summarized in Table 1.

TABLE 1—ANALYSES OF PRODUCTS OBTAINED THROUGH INTERACTION OF VARYING RATIOS OF  $\text{NaX}$  AND  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ 

	Calculated for $\text{AlX}_3$	Ratios of Reactants		
		1 Dye : $\frac{1}{3}\text{AlCl}_3$	2 Dye : $\frac{1}{3}\text{AlCl}_3$	1 Dye : $\frac{2}{3}\text{AlCl}_3$
Per cent Al.....	2.67	2.88	2.77	2.91
Per cent X.....	97.33	97.05	97.48	96.33
	100.00	99.93	100.25	99.24

The agreement between observed and calculated values is not perfect, yet it is on the whole rather good when one considers that the rinsing of the precipitate must strike a balance between two probable errors. Insufficient washing may result in contamination of the product with Orange II, whereas excessive washing might be expected to hydrolyze the salt, giving a product too low in dye and too high in aluminum. At any rate it seems safe to assume that the figures just quoted indicate a relationship other than coincidental between the quantities of dye radical and aluminum present in the products so formed.<sup>9</sup>

Weiser and Porter<sup>10</sup> accounted for the precipitate formed when a solution of aluminum chloride is added to a solution of Orange II by calling it "a mixture of hydrous alumina gel and Orange II acid," "due to the simultaneous hydrolysis of the two salts, one of a weak, slightly soluble acid with a strong base, and the other of a slightly soluble base with a strong acid." This explanation is founded upon two erroneous assumptions. The free acid of Orange II is neither a weak acid nor is it slightly soluble. We shall deal with both of these points more specifically in a moment. It is sufficient to remark now that the free acid is considerably more soluble than the dye itself and that in the experiments just discussed the dye solutions employed were far from saturated. Even had these assumptions been correct it is difficult to see how equivalent quantities of dye acid and alumina gel could have been carried down under all three sets of conditions under which we worked.

<sup>9</sup> Since this paper was presented these preparations have been repeated by the method hereafter described in connection with the  $\text{HX}-\text{AlCl}_3$  interaction—a method which gives a crystalline product and obviates the necessity of washing. The agreement between observed and calculated analyses is somewhat better than in the case of the values here recorded.

<sup>10</sup> J. Phys. Chem., **31**, 1704 (1927).

## II. THE FREE ACID OF ORANGE II

The free acid of Orange II used in the experiments which we will describe hereafter was prepared and purified according to the method of Sisley.<sup>11</sup> Briefly described the method consists essentially in refluxing Orange II with a large excess of strong mineral acid and filtering off the precipitated dye acid which is still contaminated with some of the dye. After drying to remove HCl the precipitate is extracted with a mixture of alcohol and ether and reprecipitated by the addition of a large excess of ether. When dry, the new precipitate is again extracted, but this time with ethyl alcohol. The dye acid is finally precipitated with a large excess of ether, filtered off and air-dried. It is thus obtained in the form of minute reddish-brown, needle-like crystals carrying four molecules of water of crystallization.

It may be well to discuss at this point several of the properties of the dye acid, for we have already had occasion to refer to them and shall do so again hereafter.

Sisley<sup>12</sup> determined the solubility of the dye acid in water and in varying concentrations of hydrochloric acid at 19° C. His figures are reproduced in Table 2. The first two columns are Sisley's; the other two columns have been calculated by us for convenience in reference.

TABLE 2—SOLUBILITY OF  $HX \cdot 4H_2O$  IN WATER AND HCl SOLUTIONS AT 19° C.

Concentration of HCl, Grams per Liter	Solubility of $HX \cdot 4H_2O$ Grams per Liter	Normality, HCl	HX Grams per Liter
0	174.4	0.0	142.8
1	140.6	0.027	115.2
5	88.7	0.137	72.6
10	69.7	0.274	57.1
20	9.7	0.548	7.9
30	1.89	0.822	1.55
40	0.42	1.096	0.33
50	0.27	1.37	0.22

Working at a room temperature of 25° C., we attempted an approximate check on Sisley's figures by preparing saturated solution of dye acid in distilled water and in tenth-normal hydrochloric acid. With dis-

<sup>11</sup> Bull. soc. chim. [3] 25, 862 (1901).

<sup>12</sup> Loc. cit.



tilled water we were unable to obtain a solution in equilibrium with the solid acid. The acid behaved very much like sugar, continuing to dissolve until a solution of sirupy consistency was obtained. The solution could actually be drawn into a thread with a glass rod. After about 25 gm. of acid had been added to approximately 60 cc. of water the project was abandoned. With tenth-normal hydrochloric acid a saturated solution was obtained. Ten cubic centimeters of the solution were made up to 1 liter and 20 cc. aliquots were titrated with  $\text{TiCl}_3$ . The HX content was found to be 57.1 gm. per liter. The figure obtained by plotting Sisley's first four values, drawing a smooth curve through them, and dropping perpendiculars at a tenth-normal concentration of HCl is 82.7 gm. of HX per liter. We have not been able to account for the large discrepancy between his results and our own. Unfortunately he does not state how his determinations were made. It is evident, however, that the dye acid is extremely soluble in pure water solution and quite soluble even in tenth-normal hydrochloric acid.

We have not succeeded in crystallizing the dye acid from water nor from dilute hydrochloric acid solutions, although it did crystallize from 20 per cent HCl solution.

Sisley<sup>13</sup> also remarked the apparent strength of the dye acid, as evidenced by the comparatively large excess of mineral acid necessary to free it from its sodium salt. His figures are presented in Table 3.

TABLE 3

Concentration HCl, Per Cent	Equivalents HCl per Equivalent Orange II	Orange II Decomposed, Per Cent	Orange II Undecomposed, Per Cent
0.4	1.07	no precipitate	no precipitate
1	2.14	no precipitate	no precipitate
2	4.28	no precipitate	no precipitate
2.5	5.35	46.2	53.8
3	6.42	58.5	41.5
4	8.56	78.1	21.9
5	10.70	79.4	20.6
10	21.40	80.9	19.4
15	32.10	87.5	12.5
20	42.80	97.4	2.6

As a further check upon this point small quantities of dye acid and of dye were carefully purified for the purpose of preparing solutions to

<sup>13</sup> *Loc. cit.*

be investigated potentiometrically. The dye acid, prepared as already described, was dissolved in warm alcohol. Ether was then carefully added little by little in such manner that any dye acid precipitated was redissolved before the addition of more ether. When it seemed probable that more ether would cause a permanent precipitate the flask containing the mixture was loosely stoppered with a cork stopper and allowed to stand for several days. The dye acid crystallized in large, nearly black needles which reflected a greenish sheen. Some of the crystals were over a centimeter in length and about half the diameter of a pencil lead. After being washed with ether and air-dried they were analyzed, yielding a moisture content of 9.92 per cent and an HX content of 90.13 per cent. These figures agree well with the theoretical values for  $\text{HX} \cdot 2\text{H}_2\text{O}$ .

	Calculated for $\text{HX} \cdot 2\text{H}_2\text{O}$	Found
Per cent HX.....	90.11	90.13
Per cent $\text{H}_2\text{O}$ .....	9.89	9.92
	100.00	100.05

The dye itself was crystallized, first from NaCl solution and then from alcohol.

Solutions of the dye and dye acid were made up and carefully adjusted to a normality of exactly 0.01. The concentrations were checked by titration against  $\text{TiCl}_3$ .

The solutions were then placed in Bureau of Standards burettes and mixtures prepared for hydrogen-ion measurement.

The hydrogen-ion readings were made with a Leeds-Northup student type potentiometer outfit using a quinhydrone electrode and a saturated calomel cell. The quinhydrone electrode was chosen because of the convenience and rapidity with which it can be handled and with the idea of avoiding any effect which might be produced by the reduction of dye at the hydrogen electrode.<sup>14</sup> The quinhydrone was prepared according to the method of Biilmann and Lund<sup>15</sup> and twice recrystallized from distilled water slightly acidified with acetic acid. At the time the readings were made the outfit was checked against an M/20 solution of carefully purified acid potassium phthalate. The pH value of 3.96

<sup>14</sup> We are now arranging a comparative study of the action of the hydrogen and quinhydrone electrodes with Orange II solutions.

<sup>15</sup> Ann. chim., (9) 16, 321 (1921).

obtained agreed well with the value of 3.974 reported by Clark and Lubs.<sup>16</sup> All pH values were calculated by means of the factors and cell constants tabulated by Clark.<sup>17</sup> The results obtained are summarized in Table 4.

TABLE 4.—pH VALUES OF HX SOLUTIONS AND HX—NaX SOLUTIONS AT 32.5° C.

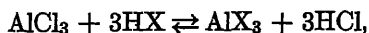
Composition of Solution, cc.			pH	HX Equivalents per Liter $\times 10^{-2}$	$[\text{H}^+] \times 10^{-2} *$
0.01 N HX	0.01 N NaX	$\text{H}_2\text{O}$			
10	.....	.....	2.05	1.0	.891
8	2	.....	2.14	0.8	.725
5	5	.....	2.31	0.5	.490
2	8	.....	2.75	0.2	.178
8	.....	2	2.15	0.8	.708
5	.....	5	2.32	0.5	.479
2	.....	8	2.66	0.2	.219

\* On the assumption that  $\text{pH} = \log \frac{1}{[\text{H}^+]}$

The results on the water dilutions are not strictly comparable to those obtained with the NaX—HX mixtures, for in the one case we are considering solutions of varying ionic strength and in the other, of constant ionic strength. Another factor which might slightly affect the results is the possibility that at high dilutions the hydroxyl of the naphthol group may come into play. Nevertheless we can conclude with some certainty that Orange II is a practically neutral salt—a fact which supports the contention that the dye acid is a strong acid.

### III. INTERACTION OF HX WITH $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

It had already been noted in our laboratory, though not previously recorded in the literature, that aluminum chloride solution forms a precipitate when added to a solution of the free dye acid. It seemed that this phenomenon might be reasonably accounted for by the equation:



where the product  $\text{AlX}_3$  is but slightly soluble. As a test of that hypothesis the present investigators prepared two products.

<sup>16</sup> J. Biol. Chem., **25**, 479 (1916).

<sup>17</sup> "The Determination of Hydrogen Ions," The Williams & Wilkins Co., Baltimore, 3rd Ed., 672, 674 (1928).

Quantities of reagents and volumes employed were approximately equivalent to those used in examining the  $\text{NaX}-\text{AlCl}_3$  interaction. The *equivalent* ratios employed were 2 aluminum : 1 acid and 1 aluminum : 1.5 acid. The procedure was varied as follows: The dye acid solution was heated to boiling and the aluminum chloride solution added slowly with stirring so that little or no precipitate remained undissolved in the hot liquid. The solution was filtered hot and the product began to crystallize as soon as the liquid began to cool. Almost the entire product crystallized in minute, orange-yellow needles, although a few leaflets could be seen. The crystals were filtered out by means of suction and then allowed to air-dry. The dry filter cakes had the appearance of felt. Analyses of these products are presented in Table 5.

TABLE 5—ANALYSES OF PRODUCTS OBTAINED THROUGH INTERACTION OF VARYING RATIOS OF HX AND  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

	$\frac{2}{3}\text{AlCl}_3 : 1\text{HX}$			$\frac{2}{3}\text{AlCl}_3 : 1.5\text{HX}$		
	No. 1	No. 2	Average	No. 1	No. 2	Average
Per cent $\text{H}_2\text{O}$ ....	20.36	20.26	20.31	16.88	16.94	16.91
Per cent Al.....	2.13	lost	2.13	2.24	2.20	2.22
Per cent X.....	77.62	76.66	77.64	80.82	80.73	80.78
	100.11	.....	100.08	99.94	99.87	99.91

In Table 6 these average values are reduced to a dry basis and compared with the calculated values for  $\text{AlX}_3$ . The agreement is rather good.

TABLE 6—VALUES OF TABLE 5 REDUCED TO DRY BASIS AND COMPARED WITH CALCULATED VALUES

	$\frac{2}{3}\text{AlCl}_3 : 1\text{HX}$	$\frac{2}{3}\text{AlCl}_3 : 1.5\text{HX}$	Calculated for $\text{AlX}_3$
Per cent Al.....	2.67	2.66	2.67
Per cent X.....	97.42	97.15	97.33
	100.09	99.81	100.00

## IV. INTERACTION OF HX WITH HYDROUS ALUMINA GEL

Marker and one of us<sup>18</sup> reported the preparation of a product containing equivalent quantities of aluminum and dye radical through the interaction of dye acid and alumina gel. Unfortunately the exact procedure followed was not described.

Weiser and Porter<sup>19</sup> have contended that the product obtained was a mixture of dye acid and gel and have accounted for the equivalency of components by assuming that equivalent quantities of dye acid and gel had been suspended in water and boiled, and that on cooling the solid matter had been filtered off and analyzed. They say:

"If the alleged compound is merely a mixture of gel with the Orange II acid crystals, why does the composition correspond to that of a chemical compound? The answer is that it does not unless the two insoluble substances, the gel and the insoluble acid, are mixed in the theoretical ratio and the analysis made for that ratio. We are forced to the conclusion that this unfortunate procedure was followed by Marker and Gordon."

Weiser and Porter, however, offer no analyses to substantiate their assertions, although they do report some qualitative experimental work. They say:

"In every case, the presence of crystals was observed in accord with the statements of Marker and Gordon. However, the crystals were not an aluminum salt but were merely the free acid of Orange II. A particularly striking crop of crystals was obtained by heating and cooling the mixture. . . . There is no doubt whatsoever that the crystals formed in the presence of the gel are the free acid. . . ."

In this connection they discuss some qualitative observations on the behavior of the crystals which we shall have occasion to refer to presently.

As a matter of fact the product previously investigated by Marker and one of us had been prepared as follows: A quantity of hydrous aluminum gel was added to a solution containing dye acid in considerable excess of the quantity calculated as necessary for reaction with the aluminum. The mixture was boiled and then filtered hot. As the clear filtrate cooled, needle-like crystals separated from it. These crystals which Weiser and Porter designate as crystals of dye acid constitute the product analyzed by Marker and found to contain equivalent quantities of dye radical and aluminum.

As a check upon the accuracy of this previous examination, the present investigators repeated the preparation, employing a small excess

<sup>18</sup> Marker and Gordon: *Ind. Eng. Chem.*, **16**, 1186 (1924).

<sup>19</sup> *J. Phys. Chem.*, **31**, 1704 (1927).

of dye acid over that calculated as equivalent to the alumina gel used. The mixture was filtered hot and the crystals which separated from the clear filtrate upon cooling were filtered with suction, air-dried for several days, and analyzed. The results were as follows:

	Found			Average Reduced to Dry Basis	Calculated for $AlX_3$
	No. 1	No. 2	Average		
Per cent $H_2O$ ....	19.62	19.64	19.63	.....	.....
Per cent $Al$ .....	2.21	2.19	2.20	2.74	2.67
Per cent $X$ .....	78.03	78.03	78.03	97.20	97.33
	99.86	99.86	99.86	99.94	100.00

Taken in conjunction with the already-presented data bearing upon the solubility and strength of the dye acid, these facts seem to furnish adequate comment upon the remark of Weiser and Porter<sup>20</sup> that, "Since Marker and Gordon assume an appreciable solubility of the alleged salts, a simple consideration of well-established laws of the kinetics of chemical reactions should have suggested the improbability of forming a salt from the much less soluble gel and a weak, slightly soluble acid."

#### V. OBSERVATIONS UPON THE BEHAVIOR OF THE SUPPOSED ALUMINUM COMPOUND

It will be noted that in none of the preceding tabulations have we assigned a definite degree of hydration to the crystals obtained. We have refrained from doing so for two reasons. Firstly, the indications are that the product obtained by allowing a boiling solution of  $AlX_3$  to cool and crystallize, consists of a mixture of hydrates. The product usually consists almost entirely of fine, needle-like crystals, but these crystals vary in size and color, depending upon the concentration and temperature of the solution from which they separate. Often a few leaflets may also be seen, especially if the mother liquor is highly concentrated and rather acid.

Secondly, it is evident that the hydrates which precipitate from solution are not stable in contact with air at room temperature. As an example we present in Table 7 two series of determinations made upon samples prepared under the same conditions, but exposed to the air for different intervals. The first was made after the product had been air-dried for three days; the second after about six weeks. Calculated values for two hypothetical hydrates are included for purposes of comparison only.

<sup>20</sup> J. Phys. Chem., **31**, 1704 (1927).

TABLE 7—ILLUSTRATING VARYING WATER CONTENT OF CRYSTALS PREPARED.

	Exposed to Air 3 days	Calculated for $\text{AlX}_3 \cdot 14\text{H}_2\text{O}$	Exposed to Air 6 weeks	Calculated for $\text{AlX}_3 \cdot 10\text{H}_2\text{O}$
Per cent $\text{H}_2\text{O}$ ...	20.31	20.01	15.07	15.16
Per cent Al.....	2.13	2.14	2.28	2.26
Per cent X.....	77.64	77.85	82.61	82.58
	100.08	100.00	99.96	100.00

Our experience with moisture determinations on these salts leads us to doubt whether there is any distinct hydrate, stable over the usual range of atmospheric temperature and humidity. We have not, however, investigated this point carefully.

The crystals of  $\text{AlX}_3$ , like those of the dye acid, retain their form under drying to constant weight at  $120$ – $125^\circ \text{C}$ . The color, however, changes to a dark, reddish brown. The anhydrous crystals are hygroscopic and change color as they regain moisture, through red to reddish orange. The compound decomposes somewhere between  $145^\circ$  and  $155^\circ \text{C}$ . Sisley<sup>21</sup> noted that the dye acid also decomposes at about  $150^\circ \text{C}$ .

The crystals cannot be *totally* redissolved in pure water nor in 95 per cent ethyl alcohol. The liquid takes on the characteristic color of the dye, the crystalline form disappears and a pulverulent orange-yellow solid phase remains. If a small amount of  $\text{HCl}$  or dye acid or a rather larger amount of  $\text{AlCl}_3$  is added to the liquid, considerable quantities of crystals will dissolve without residue upon heating. The salt is considerably more soluble in ethyl alcohol than in water.

This should not be taken to mean that none of the salt dissolves in pure water or in 95 per cent alcohol. If either of these liquids is heated with an excess of the crystals and filtered hot, crystals will again separate from the clear filtrate upon cooling. No doubt these phenomena form the basis for the statement of Weiser and Porter<sup>22</sup> that the crystals (which they believed to be crystals of the dye acid) can be dissolved from the gel with hot water or alcohol, as well as for their further assertion that, "if the (water) solution is filtered while hot the needle crystals of the free acid separate from the filtrate on cooling."

It is a rather tedious matter to prepare in this manner sufficient salt for a complete analysis, but the simple expedient of igniting a few of the crystals and noting the residue of  $\text{Al}_2\text{O}_3$  remaining would have revealed to them their error. An analysis performed by us upon a sample obtained in this way gave the following results:

<sup>21</sup> Bull. soc. chim. (3) 25, 862 (1901).

<sup>22</sup> Loc. cit.

	Found			Average Reduced to Dry Basis	Calculated for $AlX_3$
	No. 1	No. 2	Average		
Per cent $H_2O$ . . . .	19.67	19.59	19.63	.....	.....
Per cent Al . . . . .	2.03	2.04	2.04	2.54	2.67
Per cent X . . . . .	78.26	78.38	78.32	97.45	97.33
	99.97	100.01	99.99	99.99	100.00

The explanation which seems to us to account most plausibly for the phenomena just discussed is that in pure water or in 95 per cent alcohol the salt partially hydrolyzes, due to its slight solubility in the cold. If, however, some substance which might be expected to suppress hydrolysis or to dissolve the hydrous alumina so formed is added, complete solution results upon heating.

Under these circumstances it seemed to us useless to attempt any exact solubility determinations, and we have contented ourselves with the qualitative observations just made. It is obvious from what we have already said that the solubility of the salt increases greatly with increasing temperature. It is also evident that the previous assumption of one of us and Marker that the true solubility of the salt could be calculated from the amount of dye radical present in a solution in equilibrium with the solid phase was not strictly correct.

The needle-like crystals obtained from alcoholic solution are larger than those which separate from water, and deep red in color. On this account we considered the possibility that the liquid of hydration might in this case be alcohol. A sample of salt crystallized from alcohol containing a small amount of  $AlCl_3 \cdot 6H_2O$  in solution was analyzed with the following results:

	Average of Duplicate Determinations		
	Found	Reduced to Dry Basis	Calculated for $AlX_3$
Per cent loss of weight on drying . . . . .	17.52	.....	.....
Per cent Al . . . . .	2.21	2.68	2.67
Per cent X . . . . .	80.34	97.40	97.33
	100.07	100.08	100.00



About three drops of the liquid of hydration was distilled from a small sample of the crystals into a receiver containing about 0.5 cc. of distilled water. When submitted to the iodoform test after the manner recommended by Mullikan,<sup>23</sup> the liquid gave a decided test for alcohol.

Unfortunately, the entire lot of crystals was exhausted in other tests before we had an opportunity to make a refractometric reading upon the liquid of hydration. Another sample of somewhat smaller crystals was prepared from alcohol containing a slight excess of HX in solution. The analysis was as follows:

	Average of Duplicate Determinations		
	Found	Reduced to Dry Basis	Calculated for AlX <sub>3</sub>
Per cent loss of weight on drying.....	15.60	.....	.....
Per cent Al.....	2.23	2.64	2.67
Per cent X.....	82.13	97.31	97.33
	99.96	99.95	100.00

A few drops of the liquid of hydration examined in an Abbé refractometer at 27° C. gave a reading of 1.338. Since at 28° C. water has an index of 1.33219 and ethyl alcohol an index of 1.35721, it seems that the liquid of hydration must be largely water.

In the hope of discovering a suitable solvent for cryoscopic determinations we tested the solubility of the aluminum salt in a number of organic liquids. In none of the following liquids was the compound sufficiently soluble to impart an appreciable tint: benzene, toluene, petroleum ether, hexane, acetone, carbon tetrachloride, carbon disulfide, acetone. Methyl alcohol acts similarly to ethyl alcohol.

To dry ethyl ether, the anhydrous salt imparts no tint. Both the aluminum salt and the dye acid are precipitated from alcoholic solution by the addition of an excess of ether. The method of Sisley for the preparation of the dye acid makes use of this fact. We also found that the anhydrous dye acid is insufficiently soluble in dry ether to color it.

Wet ether is faintly colored by the crystalline salt. This partially confirms the statement of Weiser and Porter<sup>24</sup> that, "on shaking with ether the crystals dissolve, leaving the gel in the water layer and the

<sup>23</sup> "Identification of Pure Organic Compounds," John Wiley & Sons, Inc., New York, 1st Ed., 1, 166 (1914).

<sup>24</sup> J. Phys. Chem., 31, 1704 (1927).

ether layer is colored yellow." We found, however, that if a small portion of the wet ether layer which has been colored in this manner is drawn off and shaken with a comparatively large quantity of distilled water the color is extracted by the water layer, leaving the ether layer water-white. There is no adequate basis for the implication that ether will extract dye acid from the aluminum salt or even from a mixture of dye acid and alumina gel.

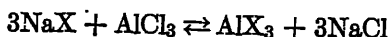
## VI. CONCLUSIONS FROM PRESENT STUDY OF ALUMINUM-ORANGE II PRODUCTS

The facts we have just set forth seem to leave no room for doubt that the compound which, for convenience, we have designated  $AlX_3$ , really exists. In view of the fact that the dye itself has been shown to be a practically neutral salt, and the dye acid to be a strong acid, it is more than improbable that the addition of Orange II solution to a solution of  $AlCl_3$  could give rise to hydrolysis which would result in a heavy precipitate of hydrous alumina. Even if such a precipitation did take place, the high solubility of the dye acid forbids the assumption that it is also precipitated. If it be contended that hydrous alumina is precipitated and that it carries down the dye acid by adsorption, there still remains the phenomenon of dye radical and aluminum equivalents obtained under a wide variation of proportions between the original reactants. If adsorption is assumed, it is necessary to assume adsorption of equivalents—which differs from compound formation only in nomenclature.

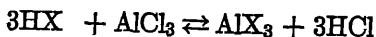
None of the other products which we have discussed was obtained under conditions which by any possibility admit an explanation involving the assumption of hydrous alumina precipitation.

There is, then, firstly, the impossibility of accounting for all the facts on the basis of any hypothesis other than that of compound formation. Secondly, there is the fact that nine products prepared under varying conditions and reported in this paper, as well as a few duplications in procedure unreported here, all showed upon analysis equivalent quantities of aluminum and dye radical. Thirdly, there is the fact that these products can be crystallized both from aqueous and from alcoholic solution—crystallization being one of the ancient and honorable criteria of the true chemical compound.

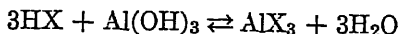
Our experiments indicate that the reactions represented by the equations:



and



take place either in cold or in hot solution. There is no reason to believe that the reaction:



does not also take place in the cold. We have conducted it in the hot because of the much greater solubility of  $\text{AlX}_3$  in hot solution, which affords an opportunity to obtain a relatively concentrated, absolutely gel-free filtrate from which the product can be crystallized by cooling.

It is obvious, therefore, that the earlier experiments of Marker and one of us<sup>25</sup> were conducted under conditions which afforded ample opportunity for compound formation. (In those experiments portions of alumina gel were treated with Orange II solutions, to which had been added varying quantities of mineral acid. The systems were then digested at 100° C. for several hours with frequent shaking.)

It is possible that, in the cold, compound formation may be limited by the formation of a coating of slightly soluble  $\text{AlX}_3$  over the gel particles so that true equilibrium is not obtained or is attained but slowly. This point has not been thoroughly investigated. Such a phenomenon does not, however, constitute adsorption within the true meaning of the term.

We do not believe that the results of an investigation of one dye and one hydrous oxide justify us in drawing any broad general conclusions on the subject of interaction between dyes and gels. We are continuing the study and are at present investigating the interactions  $\text{NaX}$  and  $\text{HX}$  with ferric salts and hydrous ferric gel. We feel safe in saying, however, that the advisability of taking into consideration the possibility of complications introduced by chemical reaction into dye-gel adsorption studies has been clearly indicated.

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<sup>25</sup> Marker and Gordon: *Ind. Eng. Chem.*, **16**, 1186 (1924).



# THE APPARENT SPECIFIC GRAVITY AND MOISTURE CONTENT OF CLAY

BY FRANK K. CAMERON AND RICHARD A. LINEBERRY

## I. INTRODUCTION

IF a solid particle be surrounded by a film of water, the "effective pressure" at a particular point of the film is proportional to the curvature and to the sum of two surface tensions, the liquid-gas and the liquid-solid.<sup>1</sup>

The effective pressure is, therefore, dependent upon the radius (or radii, if other than a sphere) of the particle and may become large for very small particles. The surface tensions are appreciably modified by change in temperature or the addition of a solute. The liquid-gas surface tension is independent of the nature of the solid. But the liquid-solid surface tension is very greatly affected by the inherent nature of the solid, its adsorption capacity, adhesion, or wettability. The properties of the film are, therefore, dependent upon the nature of the solid, its size, and its shape.

Consider now an aggregate of many particles of small radii, to which a small amount of water has been added, insufficient to form a continuous film over each of the particles. The particles will gather into a rounded mass, or ball, with the water forming a film over the whole. If more water be added gradually, the aggregate will break into smaller aggregates, each with a film more intensely held, because of diminished radius. In breaking into smaller aggregates the sum of the smaller volumes will increase, perhaps faster, even, than the increase in weight, and the apparent specific gravity of the whole mass may decrease with increasing addition of water. There comes a point, however, at which sufficient water will be added to form a film about each particle and a quite different state of affairs obtains. The films touch each other, coalesce, become more or less perfectly continuous, rounded over the grains and approaching the shape of catenoids between the grains. The dominating force holding the mass together may be the effective pressure

<sup>1</sup> For a valuable discussion of the pressures in films in soils see U. S. Dept. Agr. Bull., 10 (1897); Briggs: "The Mechanics of Soil Moisture."

in the catenoid surfaces, but the adsorption or adhesion between solid and liquid is always far from negligible. As the films thicken with continued addition of water, the curvature of the catenoid lessens, the binding power of the catenoid surfaces lessens, and the interstices become filled with water. The weight of the mass increases faster than the volume and the apparent specific gravity rises to a maximum corresponding to the point at which the maximum amount of water that can be in the film form is in this form. With further additions of water, the apparent specific gravity again falls. If the adsorption factor between liquid and solid is large, tending to lessen the volume increase with additions of water, the apparent specific gravity rises rapidly. With solids not so readily wetted, the increase in apparent specific gravity is less pronounced. Experimental illustrations of these views and discussion of some of the implications follow.

## II. THE APPARENT SPECIFIC GRAVITY OF CLAYS

Eight clays from different deposits in North Carolina were dried and portions of them ground. Apparent specific gravity determinations were made by weighing portions before and after moistening and thorough mixing in a standard glass vessel of about 40 cc. capacity. The absolute magnitudes having no intrinsic value, it is convenient to record the ratio of the apparent specific gravities of the moistened samples to those for the dry samples. Comparisons can thus be made more readily. The results for these eight clays, ground to pass 100-mesh, are assembled in Table 1 and are charted in Fig. 1. It will be observed that the curves

TABLE 1.—RATIO OF APPARENT SPECIFIC GRAVITY OF WET TO DRY CLAY WITH VARYING WATER CONTENT.

Clays ground to 100 mesh and determinations made on 100-gram samples

Water Added, Cubic Centimeters	Clay 1	Clay 2	Clay 3	Clay 4	Clay 5	Clay 6	Clay 7	Clay 8
10	1.61	0.90	0.90	0.97	1.20	1.42	1.32	1.22
20	1.52	0.95	1.09	1.06	1.30	1.45	1.42	1.46
30	1.47	1.14	1.27	1.23	1.59	1.31	1.42	1.66
40	2.72	1.66	2.58	2.63	2.49	2.42	2.32	1.67
50	2.95	2.50	2.55	2.61	2.54	2.50	2.45	3.20
60	2.95	2.56	2.49	2.53	2.48	2.51	2.31	3.57
70	2.84	2.50	2.41	2.46	2.40	2.40	2.17	3.49
80	.....	2.48	.....	2.30	2.30	.....	2.14	.....

are all of the same general character. Until a moisture content of 2.5 per cent, more or less, is attained, there is no great change in apparent

specific gravity. This portion of the curve is, relatively speaking, rather flat. In each case, considerable "balling" of the mass occurred on mixing the water with the dry powder; obtaining a fair sample for the determination presented such difficulty that the experimental error must have been

relatively large. Further additions of water promptly brought a large increase in the apparent specific gravity, a maximum being attained with the addition of 35 to 55 cc. water to 100 gm. of dry sample. Yet further additions of water brought a slow decrease in apparent specific gravity and very soon free water could be extruded by

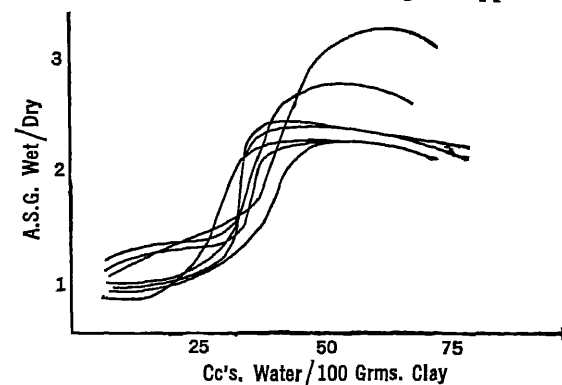


FIG. 1.—Ratio of the Specific Gravities of a Wet Clay to a Dry Clay, with Varying Moisture Content.

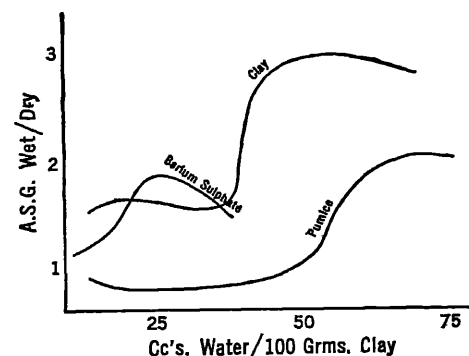


FIG. 2.—Comparison of Apparent Specific Gravity-Moisture Content Curves for a Plastic Clay and a Non-plastic Pumice.

squeezing the mass between the fingers. The determinations at the maximum apparent specific gravity have been made with a fair accuracy. The results are readily reproducible in this region.

In Table 2 and Fig. 2 are shown the data obtained for ground pumice and precipitated barium sulfate. For comparison are also given the data for one of the clays. Apparently, the curve for barium sulfate goes through a maximum, but the range

of observations is too narrow to justify definite conclusions. But there can be no possible doubt about the facts for the pumice. A relatively large addition of water was required before attaining any marked increase in apparent specific gravity, and over this range the "balling" phenom-

enon was very pronounced. The maximum finally attained was noticeably less than with the clays. It appeared that the pumice was less readily wetted than the clays.

TABLE 2.—COMPARISON OF RATIOS OF APPARENT SPECIFIC GRAVITIES, WET AND DRY, FOR CLAY 1, PUMICE GROUND TO 100 MESH, AND PRECIPITATED BARIUM SULFATE

Water Added, Cubic Centimeters	Clay 1	Pumice	Barium Sulfate
10	1.61	0.65	1.24
20	1.52	0.71	1.84
25			1.57
30	1.47	0.70	
40	2.72	0.75	
50	2.95	0.94	
60	2.95	1.84	
70	2.84	2.00	
80		1.96	

In Table 3 are data for experiments where solutions of sodium chloride or of calcium chloride were used instead of water. The corresponding

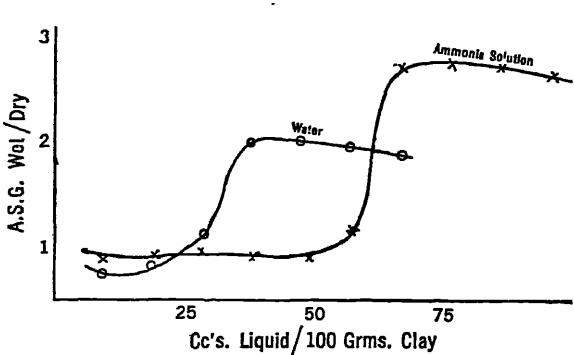


FIG. 3.—Comparison of the Effects of Water and of Concentrated Ammonia Solution, respectively, on the Apparent Specific Gravity of a Clay.

ing curves are similar, but the addition of the salt raised the apparent specific gravity, the maximum attained being higher than for pure water. Calcium chloride was more effective than sodium chloride. Qualitatively, at least, the effect can be associated with an increase in the gas-

liquid surface tension on the catenoids. We have made attempts at finding quantitative relations, but finding the amounts of selective adsorption on the solids and the effect on the liquid-solid surface tensions are factors beyond our power at present.

Concentrated ammonia solution (approximately 26 per cent  $\text{NH}_3$ ) gave a remarkable curve as shown in Fig. 3. The range over which the



balling phenomenon was observed was much wider than with water, and the maximum apparent specific gravity attained was noticeably higher than with water.

TABLE 3.—RATIO OF APPARENT SPECIFIC GRAVITY OF WET CLAY TO DRY CLAY WITH VARYING AMOUNTS OF  $\text{CaCl}_2$  AND  $\text{NaCl}$  SOLUTIONS

Clays ground to 100 mesh and determinations made on 100-gram samples

CALCIUM CHLORIDE SOLUTION, DENSITY 1.37

Solution, Cubic Centimeters	Clay 1	Clay 2	Clay 3	Clay 4	Clay 5	Clay 6	Clay 7	Clay 8
10	1.65	1.06	1.13	1.09	1.46	1.45	1.45	1.79
20	1.46	1.00	1.20	1.29	1.44	1.58	1.28	1.83
25	2.56	1.20	1.32	1.41	1.42	1.55	1.21	1.90
30	3.35	1.48	1.40	1.67	1.54	1.75	1.28	1.95
35	3.26	2.03	2.37	2.72	2.96	2.38	2.14	2.46
40	.....	2.62	2.95	3.00	2.97	2.96	2.42	4.00
45	.....	2.61	2.93	2.95	2.95	3.00	2.53	4.34
50	.....	.....	.....	.....	.....	3.01	2.47	4.24
55	.....	.....	.....	.....	.....	3.00	.....	.....

SODIUM CHLORIDE SOLUTION, DENSITY 1.03

Solution, Cubic Centimeters	Clay 1	Clay 2	Clay 3	Clay 4	Clay 5	Clay 6	Clay 7	Clay 8
10	1.57	0.90	0.99	0.97	1.33	1.41	1.28	1.38
20	1.41	1.01	1.20	1.13	1.30	1.44	1.22	1.63
25	2.65	1.15	1.24	1.10	1.40	1.43	1.16	1.79
30	3.01	1.18	1.40	1.22	2.06	1.65	1.26	1.86
35	2.99	1.20	2.56	2.18	2.52	2.28	1.91	2.13
40	.....	2.27	2.76	2.16	2.73	2.78	2.21	3.40
45	.....	2.48	2.70	.....	2.53	7.33	2.33	3.83
50	.....	2.46	.....	.....	.....	.....	2.31	3.80

Several liquids (organic compounds) which do not wet clay as readily as does water were tried with the results assembled in Table 4 and Fig. 4. The results recall that obtained by water on pumice. The charted curves are recognizably different from the clay-water complexes in that there is a much larger region where the balling takes place, and the slope of the

curve between the point where balling disappears and the maximum apparent specific gravity is attained is very much less steep. The maximum apparent specific gravity is lower than with water.

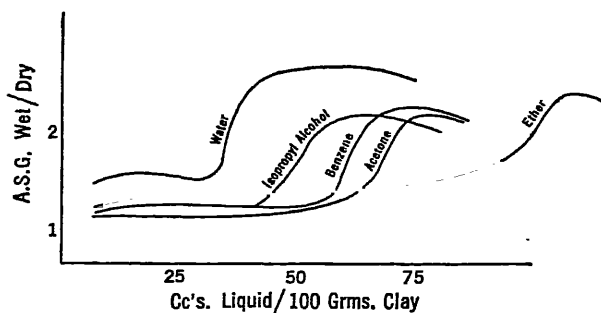


FIG. 4.—Comparison of Apparent Specific Gravity Ratios for a Clay; Plastic when Wet with Water; Less Plastic when Wet with Various Organic Liquids.

TABLE 4.—COMPARISON OF RATIO OF APPARENT SPECIFIC GRAVITY WITH VARYING AMOUNTS OF ORGANIC LIQUIDS

Clays ground to 100 mesh and determinations made on 100-gram samples

CLAY 6. RATIO OF APPARENT SPECIFIC GRAVITY OF WET CLAY TO DRY CLAY

Amount, Cubic Centimeters	Acetone	Ether	Isopropyl Alcohol	Benzene	Toluene
10	1.02	1.17	1.06	1.00	1.05
20	1.04	1.26	1.13	1.10	1.08
30	1.05	1.25	1.14	1.01	1.07
40	1.10	1.31	1.06	1.01	1.09
50	1.08	1.31	1.77	1.02	1.01
60	1.28	1.32	2.05	1.81	1.82
70	2.01	1.31	2.00	2.14	2.06
80	1.97	1.40		2.08	2.00
90	.....	1.50	.....		
100	.....	2.26			
110	.....	2.18			

To test the effect of increasing the liquid-solid boundaries, several sets of experiments were tried with ground clays of different screen separations. Data for two of these sets are given in Table 5 and are charted in Fig. 5. With clay 1 there was but little change in the extent of the region of "balling," but a marked increase in the maximum apparent specific gravity with finer texture. With clay 8 there appeared to be

TABLE 5.—EFFECT OF GRINDING ON RATIO OF APPARENT SPECIFIC GRAVITY OF WET CLAY TO DRY CLAY TO DRY CLAY WITH VARYING WATER CONTENT

Determinations made on 100-gram samples

## CLAY 1. RATIO OF APPARENT SPECIFIC GRAVITY OF WET CLAY TO DRY CLAY

Solution, Cubic Centimeters	20-mesh	40-mesh	60-mesh	100-mesh
10	1.17	1.23	1.26	1.61
20	0.96	1.10	1.07	1.52
30	1.19	1.20	1.26	1.47
40	1.54	1.65	1.96	2.72
50	1.85	2.10	2.13	2.95
60	1.82	2.08	2.07	2.95
70	.....	.....	.....	2.84

## CLAY 8. RATIO OF APPARENT SPECIFIC GRAVITY OF WET CLAY TO DRY CLAY

Solution, Cubic Centimeters	20-mesh	40-mesh	60-mesh	100-mesh
10	1.07	1.12	1.09	1.22
20	1.20	1.22	1.27	1.46
30	1.25	1.23	1.40	1.66
40	1.21	2.04	2.60	1.67
50	2.15	2.53	2.90	3.20
60	2.43	2.45	2.85	3.57
70	2.33	.....	.....	3.49

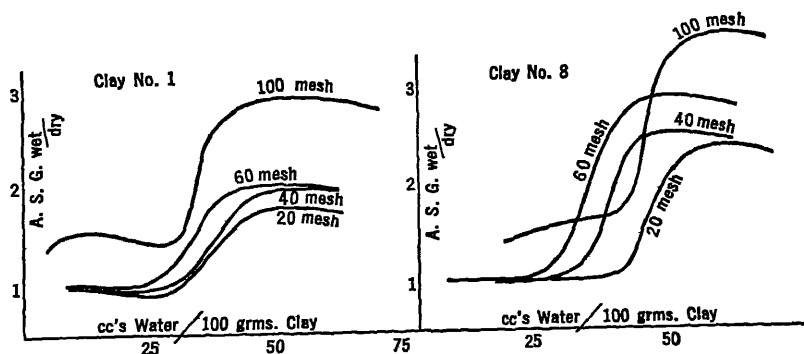


FIG. 5.—Effect of Grinding on the Apparent Specific Gravities of Two Plastic Clays.

an appreciable shortening of the region of balling as the texture became finer, from 20-mesh to 60-mesh. But the 100-mesh sample showed practically the same region of balling as the 20-mesh. The apparent specific gravity increased regularly with the increase in fineness of texture.

Cameron and Gallagher,<sup>2</sup> in studying the effect of moisture content on the apparent specific gravity of soils, found that on alternately wetting and drying the soil and plotting the results, both the wetting curves and the drying curves passed through a maximum apparent specific gravity at the same moisture content. But the drying curve lay below

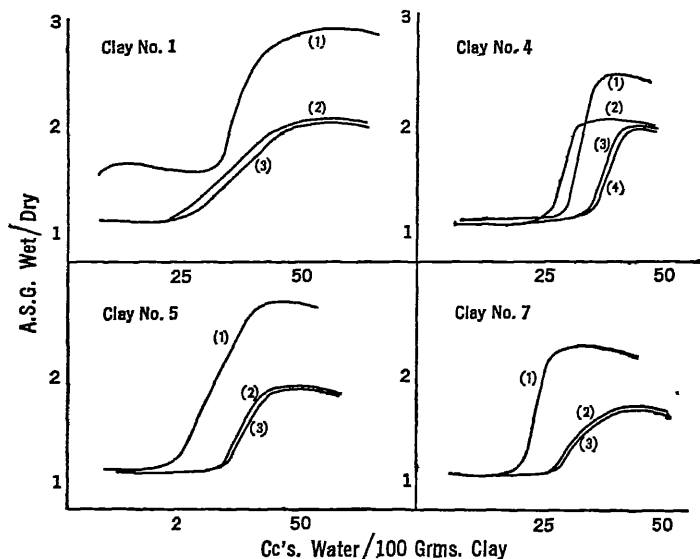


FIG. 6.—Hysteresis in Apparent Specific Gravity-Moisture Content Relations on Successive Wettings and Dryings.

the wetting curve. On repeating the process, the wetting curve lay between the two others and the drying curve still lower. But always the maximum apparent specific gravity was at the same moisture content. There was evidently a hysteresis. And successive wetting and drying produced a "natural packing," as it was denominated, since such a process is taking place in the field where a soil is always being wetted or being dried. The phenomenon is of obvious importance in soil management, and its recognition has found some use in engineering practice. In Fig. 6 is shown the curves obtained for several clays.

<sup>2</sup> Cameron and Gallagher: U. S. Dept. Agr. Bull., 50, (1908).

After a wetting curve was determined, the sample was dried at 75° C. in an electrically heated and controlled oven. The mass was then broken into lumps, and a new curve determined by adding more water and stirring. Successive curves fell below one another in order. But in each case there was more or less displacement of the maximum point, and always in the direction of a larger water content. The data, having no intrinsic value, are not tabulated here.

TABLE 6.—EFFECT OF SUCCESSIVE WETTING AND DRYING. RATIO OF APPARENT SPECIFIC GRAVITY OF WET TO DRY CLAY WITH VARYING WATER CONTENT

Clays ground to 100 mesh and determinations made on 100-gram samples

Water Added, Cubic Centimeters	Clay 1				Clay 4			
	1st	2nd	3rd	4th	1st	2nd	3rd	4th
10	1.43	1.28	1.19	1.20	0.90	0.83	0.85	0.85
20	1.32	1.14	1.15	1.13	1.01	0.94	0.92	0.98
25	1.36	1.33	1.40	1.37	1.19	1.47	0.97	1.12
30	2.19	1.85	1.95	1.83	1.20	2.03	1.02	1.67
35	2.59	2.13	2.00	2.04	2.50	2.13	1.08	2.10
40	2.56	2.09	1.97	2.00	2.46	2.11	1.71	2.06
45	.....	.....	.....	.....	.....	.....	2.17	.....
50	.....	.....	.....	.....	.....	.....	2.13	.....

Water Added, Cubic Centimeters	Clay 5			Clay 7		
	1st	2nd	3rd	1st	2nd	3rd
10	1.28	1.06	1.05	1.26	1.05	1.00
20	1.33	1.03	1.01	1.25	0.99	0.95
25	1.43	1.02	1.02	1.59	0.93	0.89
30	1.90	1.13	1.06	2.29	1.19	1.04
35	1.73	1.35	1.88	2.35	1.53	1.40
40	2.78	1.89	1.93	2.34	1.65	1.68
45	2.76	1.90	1.87	.....	1.68	1.66
50	.....	1.84	.....	.....	1.65	1.60

### III. APPARENT SPECIFIC GRAVITY AND PLASTICITY

Probably everyone knows, or thinks he knows, what plasticity is. Moreover a considerable number of people think they know the cause or causes, and many methods of measuring it have been proposed. But there is no consensus of opinion on any of these subjects. We therefore

are emboldened to offer a few considerations based on the foregoing discussion and experiments. We consider that the properties of a one-phase system like soft tar or lead are probably different in kind and resemble only superficially those of a polycomponent system like a wet clay. Hence, it would be helpful to think of the former in measures of viscosity and reserve the term plasticity as applying only to dispersed systems in which one component at least is a film-forming liquid.

Plasticity will appear in that region between the point at which there is sufficient moisture to form a film about each particle and the point at which maximum apparent specific gravity can be attained. The necessary condition for plasticity is that the liquid shall readily wet the solid; that is, that there shall be a strong adsorption or adhesion between the liquid and the solid and high surface tension in the liquid interface. Any solute which will increase this surface tension will increase plasticity and *vice versa*. With a high tension in the liquid-solid surface, this surface will not be readily broken and the solid particles will be held together firmly, even though their relative positions be greatly and roughly disturbed. This is what one means by plasticity. Referring to the charts it will be noted that the systems showing marked plasticity, the clays mixed with water or solutions of electrolytes, yielded curves with a steep slope in the region of plasticity. Also, there is a restricted region in which the "balling" phenomenon was conspicuous. There can be no doubt that in these cases there was a strong affinity between the liquid and the solid. But with the pumice, which was composed of particles as small as those of the clay, and in the experiments where organic liquids were mixed with clays, the slope was much less steep and the region of balling more extended, indicating a lesser attraction between liquid and solid.

For a correct evaluation of plasticity, therefore, it would be necessary to make quantitative estimates of the solid-liquid surface tension. This we cannot do at present. We can correlate plasticity with apparent specific gravities, however, and since these can quickly and easily be determined they may have a value for plant control methods.

It may not be amiss to point out that the plasticity of clays and similar substances, at least from the point of view here developed, does not in any way require the assumption of colloid coatings on the clay particles. If the particles be of small enough diameter, the clay itself will be a colloid. The experiments cited above, on very finely ground material, are pertinent. It is unreasonable to assume that there could have been any material increase in colloidal alumina or silica in these grindings, yet the plasticity was increased. It is quite reasonable to assume that as more surface was developed for the water to wet, the

greater the binding and that the high adsorption of water by the clay particles is a sufficient explanation.

That colloidal silica, and possibly alumina, are concomitants in the formation of kaolinite from more complex alumina silicates is true. And in some cases they very probably are present, but not necessarily always. And it is also very probable that we have in the past allowed the possibility of their presence to interfere with clear thinking, and assumed that they are necessary for plasticity, an assumption that is at least questionable.

Whatever plasticity may be, the control of it is a matter of great practical importance. In the management of soils, it is desirable that it be at a minimum. In the treatment of ceramics it is desirable to have it at a maximum. It is with a desire to provide a basis for further experimentation that the present study is recorded, rather as the story of a pioneering venture than as a finished research.

#### SUMMARY

1. Application has been made of the mechanics of a moist powder to the phenomenon of balling and to variation in apparent specific gravity.

2. Plasticity in a polycomponent system is due mainly to a high surface tension in the solid-liquid interface of the liquid film.

3. The distinction between the water content-apparent specific gravity curves for plastic substances and for non-plastic substances is easily observed.

4. It will be convenient to ascribe plasticity to polycomponent systems and not to one-component systems.

5. Apparent specific gravities can be made so readily and quickly that they may be the basis of a plant control method in the ceramic industries.

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# PROGRESS IN THE STUDY OF THE CLAY MINERALS <sup>1</sup>

BY EDGAR T. WHERRY, CLARENCE S. ROSS, AND PAUL F. KERR

The development of new methods of study in recent years is leading mineralogists to revise their views as to the nature of various classes of minerals, and in none is this revision more far-reaching than in that of the clays. As the interpretation of the colloidal phenomena exhibited by these substances may be affected by information as to their constitution, a summary of the progress which has been made thus far seems pertinent to this symposium. Details are being left for publication elsewhere.

There are, it now appears, at least three main types of clay minerals, differing fundamentally in crystal structure as revealed by X-ray examination:

1. The kaolin clays.
2. The montmorillonite clays.
3. The potash-bearing clays.

Rather unexpectedly, however, these do not differ consistently in silica : alumina ratio, but overlap considerably in this respect.

## I. THE KAOLIN CLAYS

a. Kaolinite (Johnson, 1867). Optically negative, with a very small extinction angle (around  $3^\circ$ ), acute bisectrix normal to *c*, and 2V moderate.

Chemically a hydrous aluminum silicate with  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  normally 2 : 1, but sometimes ranging up to 3 : 1, without essential change in structure. This variation in ratio is not due, as might be suspected in view of the character of most past work on clays, to analyses having been made on specimens contaminated with silica gel or other impurities, for all the materials here investigated have been subjected to the most rigorous microscopic investigation, and further studied only when their homogeneity was established.

*Important Varieties:* Halloysite, which appears to be a submicroscopically crystallized form of the same compound.

<sup>1</sup> Published by permission of the Director of the U. S. Geological Survey.

Anauxite, the high silica form resulting from the weathering of certain igneous rocks.

Beidellite, a similarly high-silica form found as gouge-clay around metalliferous veins, and apparently widespread in shale rocks and in soils.

b. "Kaolinite" (Dick, 1888); will require a new name. Optically positive with rather large extinction angle (around  $20^\circ$ ), acute bisectrix normal to b, and 2V large.

Chemically a hydrous aluminum silicate with  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  strictly 2 : 1. The best crystallized and most constant in composition of all these minerals. Rare in nature.

c. Nacrite (Breithaupt, 1832). Optically negative, with the extinction angle about  $10^\circ$ , the acute bisectrix normal to a perfect cleavage, and 2V large.

Chemically apparently identical with the preceding, but still rarer.

## II. THE MONTMORILLONITE CLAYS

Montmorillonite (Salvetat, 1847). Optically negative with a small axial angle.

Chemically the original mineral so called was a hydrous aluminum silicate with the ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3 = 4 : 1$ , and perhaps the majority of other occurrences have this ratio. Many vary from it, however, some being higher in silica, up to at least 5 : 1, while others are lower, reaching 3 : 1 or even 2 : 1, without change in structure, although with a slight alteration of the unit-cell dimensions, as shown by X-rays. In addition, MgO is frequently present, apparently as an essential constituent.

These clays are found in nature under various conditions, being present, for example, in many soils, but their most interesting occurrence is in the rock known as bentonite. This rock is now recognized to have been produced by the ejection of finely disintegrated lava from volcanoes, and the settling of the particles through the air and through water, yielding stratified beds. Under the influence of substances present in the water, the glass changes into a clay which usually has the composition and structure just described.

## III. THE POTASH-BEARING CLAYS

The clays of this type, which have as yet not been fully investigated, are known in metamorphosed bentonites, in gouge-clays of metalliferous veins (where they have often been mistakenly identified as sericite), and in altered igneous rocks. Optically these minerals differ from montmorillonite in having somewhat higher refractive indices, although

double refraction and axial angle are about the same; the pattern obtained by X-rays is, however, distinctive.

Chemically these clays are characterized by a fairly high silica-alumina ratio, perhaps averaging 3 : 1, and by the presence of several per cent of  $K_2O$ .

Although clays of the kaolin type are extensively used in the ceramic industries, those of the montmorillonite type are of greater interest to colloid chemists because they are the ones exhibiting the maximum powers of adsorption, such as are at present being put to practical use in softening water, clarifying oils, etc. From what has been stated as to the variable formula of the montmorillonite clays, it appears that the features of these clays are not so much connected with composition, in the sense of alumina-silica ratio, as with molecular structure, as brought out by X-ray study.

Further work is under way, covering the examination of many additional samples of all of these minerals, the developing of possible explanations for the failure of wide variation in composition within each type to affect the structure, and the drawing up of criteria for the recognition of the several types.

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AND  
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# THE COLLOIDAL NATURE OF SOME FINELY DIVIDED NATURAL PHOSPHATES

BY K. D. JACOB,<sup>1</sup> W. L. HILL,<sup>1</sup> AND R. S. HOLMES<sup>2</sup>

ACCORDING to Scott<sup>3</sup> and Lindgren,<sup>4</sup> practically all the phosphate minerals, including the types of calcium phosphate universally known as phosphorite and phosphate rock, are of colloidal origin. For purposes of classification, Lindgren divides minerals of colloidal origin into two broad groups: (1) the amorphous mineral gels which very frequently have been altered to such an extent that they have lost many, if not all, of the properties characteristic of colloidal materials; and (2) the meta-colloids, or recrystallized gels. The phosphate rocks, phosphorites and certain hydrated phosphates of iron and aluminum belong to the first class, while the second class includes such crystalline phosphates as apatite, vivianite, wavellite, etc.

The amorphous calcium phosphates are widely distributed and commercial deposits exist in all parts of the world. Although the commercial types of amorphous calcium phosphate have usually been altered to such an extent that they have lost practically all the physical properties characteristic of colloids, they are associated in many cases with phosphatic materials which seem to be composed of loosely cohering aggregates of extremely fine particles. It seems reasonable to suppose that at least some of these particles are colloidal in size. In this connection Elschner<sup>5</sup> has described a plastic clay-like calcium phosphate, occurring on Washington Island of the Fanning group in the South Seas, which he considers to be a true colloid.

As a part of an investigation on the composition, properties and utilization of the so-called "soft" phosphates of Florida, the authors have made a preliminary study of the colloidal nature of these materials and also of a sample of ground phosphate rock from Tennessee. The

<sup>1</sup> Fertilizer and Fixed Nitrogen Division.

<sup>2</sup> Soil Chemistry and Physics Division.

<sup>3</sup> "Brit. Assocn. Advancement Sci., Fourth *Rept.* on Colloid Chemistry," 204-43 (1922).

<sup>4</sup> Bogue's "The Theory and Application of Colloidal Behavior," 2, 445-65 (1924).

<sup>5</sup> *Kolloid-Z.*, 31, 94-6 (1922).

results obtained seem to be of sufficient interest to warrant their mention at this time.

## I. OCCURRENCE OF FINELY DIVIDED NATURAL PHOSPHATES IN THE UNITED STATES

The Florida hard rock phosphate deposits usually contain a relatively high percentage of finely divided phosphatic material classified under the general term, soft phosphate. Soft phosphate also occurs in smaller quantities in the Florida pebble phosphate deposits and to a certain extent as individual deposits in both the hard rock and pebble phosphate districts. Finely divided phosphates also occur in the Tennessee brown rock phosphate field and probably, to a certain extent, in the other phosphate deposits in this country.

Florida soft phosphate usually occurs in the form of more or less soft, white lumps and when wet exhibits the plastic, sticky characteristics of clay. It is variable in composition, but Wyatt<sup>6</sup> reports as an average analysis of 148 samples, 65.15 per cent tricalcium phosphate and 9.2 per cent oxides of iron and aluminum, the limits not being given.

During the process of preparing Florida hard rock phosphate for the market the soft phosphate present in the matrix is washed into waste ponds where it settles out along with the clay and other impurities, the finer particles concentrating at points farthest from the entrance to the pond. When the ponds become filled with waste material they are allowed to dry up and the water from the phosphate washers is turned into new ponds. These "waste-pond" phosphates, which usually vary in shade from white to a light straw color, are composed of very fine particles and when wet they are quite plastic and sticky. Upon drying they shrink and crack in the manner characteristic of materials containing high percentages of colloid. The air-dried lumps disintegrate rapidly when placed in water. The air-dried material usually contains about 40 to 55 per cent tricalcium phosphate and about 15 to 18 per cent iron and aluminum oxides. The abandoned waste ponds in the Florida hard rock phosphate district to contain several million tons of this material.

Owing to the relatively low content of phosphate and high content of iron and aluminum, it has not been considered practicable to attempt the conversion of soft phosphate into superphosphate by treatment with sulphuric or other acids. Waggaman,<sup>7</sup> and Matson<sup>8</sup> have suggested, however, that owing to the fineness of the particles it should prove a

<sup>6</sup> "The Phosphates of America," 4th Ed., 77 (1892).

<sup>7</sup> U. S. Dept. Agr., Bureau of Soils, Bull., 76, 23 pp. (1911).

<sup>8</sup> U. S. Geol. Survey Bull., 604, 101 pp. (1915).

valuable phosphate fertilizer material for direct application to certain types of soil. A small quantity has been produced annually for this purpose.

## II. EXPERIMENTAL WORK

The phosphates used in the present investigation were as follows: (1) *Waste-pond Phosphate* from an abandoned hard rock phosphate waste pond near Dunnellon, Florida; (2) *Soft Phosphate* from a natural deposit 0.5 mile east of Juliette, Marion County, Florida; and (3) *Tennessee Brown Rock Phosphate* from Mt. Pleasant, Tennessee.

The waste-pond phosphate and soft phosphate were received in the wet condition. They were dried at a temperature of 80–90° C. and crushed to pass a 10-mesh sieve. The Tennessee brown rock phosphate was a regular commercial material which had been washed and kiln-dried. It was ground to pass a 100-mesh sieve.

### PHYSICAL COMPOSITION AND PROPERTIES

In order to obtain information on the physical composition of the phosphates, samples were subjected to the procedure used by the Soil Chemistry and Physics Division of this Bureau for the mechanical analysis of soils,<sup>9</sup> the size of the particles from the different fractions being checked by means of the microscope.

The results, which are given in Table 1, show that 70 per cent of the waste-pond phosphate was composed of particles 5 microns and less in diameter, this corresponding with the clay fraction of soils, while practically the entire sample was composed of particles 50 microns and less in diameter. In the case of the soft phosphate, 39 per cent was made up of particles 5 microns and less in diameter and 44.1 per cent of particles 5 to 50 microns in diameter, the latter fraction corresponding with the silt fraction of soils. The ground rock phosphate contained 14.4 per cent of particles 5 microns and less in diameter. The high percentage of very fine material in the waste-pond phosphate is not surprising in view of the fact that this material was deposited from water suspension and consequently had already undergone a partial fractionation into fine and coarse particles.

Robinson and Holmes<sup>10</sup> state that the soil fraction designated by the American system of mechanical analysis<sup>11</sup> as clay and composed of

<sup>9</sup> Fletcher and Bryan: U. S. Dept. Agr., Bureau of Soils, Bull., 84, 16 pp. (1912).

<sup>10</sup> U. S. Dept. Agr. Bull., 1311, 41 pp. (1924).

<sup>11</sup> Fletcher and Bryan: *Loc. cit.*

# MODAL NATURE OF DIVIDED NATURAL PHOSPHATES

TABLE 1.—PHYSICAL COMPOSITION OF SOME FINELY DIVIDED NATURAL PHOSPHATES

Phosphate Material	Mechanical Fractions, Diameters of Particles in Microns					
	2000-1000	1000-500	500-250	250-100	100-50	50-5
Phosphate from waste pond near Dun- nelon, Florida.....	Per Cent by Weight 0.0	Per Cent by Weight 0.0	Per Cent by Weight 0.0	Per Cent by Weight 0.0	Per Cent by Weight 0.3	Per Cent by Weight 29.7
Soft phosphate from natural deposit near Juliette, Florida.....	1.3	2.2	2.2	5.8	5.4	39.0
Brown rock phosphate from Mt. Pleasant, Tennessee. Washed and dried material, ground to pass 100-mesh sieve.....	0.0	0.0	0.0	0.1	32.3	53.2
						14.4



particles 5 microns and less in diameter, is nearly all colloidal. According to Joseph,<sup>12</sup> in the case of certain soils the entire clay fraction may be obtained as colloid by repeated centrifuging. Some unpublished work of the Soil Chemistry and Physics Division of the Bureau of Chemistry and Soils indicates that in general approximately 90 per cent of the clay fraction of many American soils is composed of particles 2 microns and less in diameter which may be considered as mostly colloidal. On this basis, if we assume a similarity between the physical properties of finely divided natural phosphates and soils, the mechanical analyses would indicate that the waste-pond phosphate, soft phosphate and ground rock phosphate contained approximately 63, 35, and 13 per cent of colloid, respectively.

There are several other methods by means of which fairly close approximations of the colloid content of soils may be obtained without actual separation of the colloidal matter. Among these may be mentioned the adsorption of dyes, ammonia and water,<sup>13, 14</sup> and the heat of wetting.<sup>15</sup> The quantity of water adsorbed per gram of soil over 3 per cent sulphuric acid under a vacuum of 50 millimeters or less of mercury seems to give a very good indication of the quantity of colloid present, knowing first the quantity of water adsorbed per gram of extracted colloid under the same conditions. From the investigation of a number of soil colloids, Robinson<sup>16</sup> obtains an average adsorption of 0.298 gm. of water per gram of colloid, the deviation from the average being  $\pm 0.027$  gm. Using the average figure, the percentage of colloid in a soil may be expressed by the ratio

$$\frac{\text{Water adsorbed per gram of soil}}{0.298} \times 100$$

The quantity of water adsorbed per gram of material was determined for each of the three phosphates, the results being 0.174, 0.123, and 0.043 gm. for the waste-pond phosphate, soft phosphate and ground rock phosphate, respectively. Assuming again a similarity between the physical properties of finely divided natural phosphates and soils we find by the ratio given above that the apparent quantity of colloid in the materials is 58.4, 41.3, and 14.4 per cent for the waste-pond phosphate, soft phosphate, and ground rock phosphate, respectively.

<sup>12</sup> Soil Science, **20**, 89-94 (1925).

<sup>13</sup> Gile, Middleton, Robinson, Fry, and Anderson: U. S. Dept. Agr. Bull., **1193**, 41 pp. (1924).

<sup>14</sup> Robinson: J. Phys. Chem., **26**, 647-53 (1922).

<sup>15</sup> Anderson: J. Agr. Research, **28**, 927-35 (1924).

<sup>16</sup> Robinson: *Loc. cit.*

It will be noted that the quantities of colloid in the different phosphates as estimated by the two approximate methods agree quite well. These results were then checked by an actual separation of the extractable colloid by means of the supercentrifuge employing the general procedure outlined by Gile, *et al.*,<sup>17</sup> except that in no case was it necessary to use ammonia in order to disperse the colloid.

It is a well-known fact that even the so-called extractable colloid is completely separated from soils only with the greatest difficulty. Therefore in working with the phosphates the alternate processes of agitating with water and centrifuging were usually performed about twelve times. The appearance of the dispersed phase from the last extraction, however, indicated that only a small quantity of dispersible colloid remained in the coarse residue. In general, the largest quantities of colloid seemed to be obtained in the second to fifth extractions.

The colloidal solutions were concentrated by means of Chamberland-Pasteur filters and finally evaporated to dryness on the steam bath. The dry colloid was obtained in the form of more or less hard scales having approximately the same color as that of the original material. In the case of the waste-pond phosphate the colloidal material from the last extractions was concentrated separately from that of the first extractions and it was noted on drying that the colloid extracted last was softer and more friable than that extracted first. As a whole, the colloid from the waste-pond phosphate seemed to be the toughest and hardest, followed in order by that from the soft phosphate and ground rock phosphate.

The percentages of colloid obtained from the phosphates, together with the percentages estimated from mechanical analysis and water adsorption figures, are given in Table 2. The percentages of colloid, as determined by actual extraction were 60.1, 38.6, and 11.5 in the waste-pond phosphate, soft phosphate, and ground rock phosphate, respectively. These figures agree surprisingly well with the percentages estimated from the results of the mechanical analyses and water adsorption experiments, which indicates a similarity between the physical properties of phosphate colloids and soil colloids.

Although the residues from the extractions had none of the plastic, sticky properties of the original phosphates, they undoubtedly still contained some extractable colloid and possibly some non-extractable colloid.<sup>18</sup> The size of the colloidal particles extracted from the phosphates has not been determined as yet, but with the method of separation

<sup>17</sup> Gile, Middleton, Robinson, Fry, and Anderson: U. S. Dept. Agr. Bull., 1193, 41 pp. (1924).

<sup>18</sup> Fry: J. Agr. Research, 24, 879-83 (1923).

used it is unlikely that very many, if any, exceeded 1 micron in diameter, and the majority were probably 0.3 of a micron and less.

TABLE 2.—PERCENTAGES OF COLLOID EXTRACTED FROM FINELY DIVIDED NATURAL PHOSPHATES

Phosphate Material	Quantity of Colloid		
	Extracted by Means of Super- centrifuge, Per Cent	Estimated from Results of	
		Mechanical Analysis, Per Cent	Water Absorption Experiments, Per Cent
Waste-pond phosphate * . . . . .	60.1	63.0	58.4
Soft phosphate † . . . . .	38.6	35.0	41.3
Ground rock phosphate ‡ . . . . .	11.5	13.0	14.4

\* 200 gm. taken for extraction of colloid.

† 300 gm. taken for extraction of colloid.

‡ 1000 gm. taken for extraction of colloid.

It is perhaps not surprising that the waste-pond phosphate should contain such a high content of colloid, owing to the fact that it had already undergone a partial separation from the coarser particles originally present. The soft phosphate, on the other hand, was taken directly from a natural deposit, yet it contained 38.6 per cent of colloid which approximates the average colloid content of clay soils. At present it is impossible to state definitely whether the colloid content of the ground rock phosphate originated from the grinding of the hard rock, or was present as soft colloidal aggregates in the original rock. It would be surprising, however, if the simple grinding process used on this phosphate produced 12 to 14 per cent of colloid from non-colloidal material. The porous nature of Tennessee brown rock phosphate indicates that it would be practically impossible to remove, by the customary washing procedure, all the finely divided clay-like phosphate which is undoubtedly present in the interstices of the lumps of hard rock.

#### CHEMICAL COMPOSITION

Several hundred grams of each of the three phosphates were separated by sedimentation into fractions composed of particles having a range of diameter of 750 to 50, 50 to 5, and 5 to <5 microns, respectively, as checked by means of the microscope, these fractions corresponding

with the sand, silt, and clay fractions of soils as determined by the American system of mechanical analysis.<sup>19</sup> The partial chemical compositions of the original phosphates, the 5 to <5-micron fractions, and the colloid fractions are given in Table 3. The figures are all based on constant weight at 105–110° C.

In the case of the waste-pond phosphate there is a marked increase in the percentages of silica, alumina, and iron oxide and an approximately corresponding decrease in the percentages of lime, phosphoric acid, and fluorine in the colloid as compared with the original phosphate. This difference is even more pronounced with the ground rock phosphate. With both these phosphates the composition of the colloid fraction approximates that of the clay fraction much more closely than it does that of the original phosphate. On the other hand, there is no considerable difference between the composition of the original soft phosphate and the composition of its colloid fraction.

The ratio of phosphoric acid to lime remains quite constant in the original samples and the fractions of the waste-pond phosphate and soft phosphate, but increases in going from the original sample to the colloid fraction in the case of the ground rock phosphate. The ratio of silica to alumina and iron oxide remains fairly constant in the case of the waste-pond phosphate but shows considerable variation in the soft phosphate and ground rock. With each phosphate there is no constant ratio of phosphoric acid to fluorine in the fractions, the ratios increasing in going from the original sample to the colloid. The originals and fractions of soft phosphate and ground rock phosphate, except the colloid fraction of the latter, contain more fluorine than corresponds to the nuoroapatite formula,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ , a fact which has also been floted by Jacob and Reynolds<sup>20</sup> in the case of all the commercial types and grades of phosphate rock produced in the United States.

By way of comparison it is interesting to note that Robinson and Holmes<sup>21</sup> found that 45 soil colloids had the following partial composition: silica 31.84 to 55.44, alumina 16.42 to 38.28, iron oxide 4.66 to 16.67, lime 0.17 to 5.01, and phosphoric acid 0.02 to 0.65 per cent, no figures being given for fluorine. Thus in the case of soil colloids, iron oxide and alumina are by far the predominating bases and silica is the only acid radical present in any quantity, while in the phosphate colloids lime and phosphoric acid are the predominating base and acid, although considerable quantities of iron oxide, alumina and silica are also present.

Although the data presented in the present paper are too meager to

<sup>19</sup> Fletcher and Bryan: U. S. Dept. Agr., Bureau of Soils, Bull., **84**, 16 pp. (1912).

<sup>20</sup> J. Assocn. Official Agr. Chem., **11**, 237–50 (1928).

<sup>21</sup> U. S. Dept. Agr. Bull., **1311**, 41 pp. (1924).

TABLE 3.—CHEMICAL COMPOSITION OF ORIGINAL PHOSPHATES, AND CLAY \* AND COLLOID FRACTIONS EXTRACTED THEREFROM

Phosphate Material	Sample Analyzed	P <sub>2</sub> O <sub>5</sub>	CaO	SiO <sub>2</sub> †	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	IF	Ignition Loss	P <sub>2</sub> O <sub>5</sub> -CaO Ratio	Si <sub>2</sub> O-R <sub>2</sub> O <sub>3</sub> Ratio	P <sub>2</sub> O <sub>5</sub> -IF Ratio
		Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent			
Waste-pond phosphate...	Original.....	23.48	30.89	18.10	11.77	3.01	1.81	7.34	0.760	1.154	12.972
	Clay fraction..	22.01	20.55	19.47	12.85	4.23	1.30	.....	0.745	1.130	16.184
	Colloid.....	18.12	23.73	24.80	16.29	5.12	0.84	8.35	0.704	1.161	21.571
Soft phosphate.....	Original.....	31.80	41.01	9.80	5.91	1.54	3.33	5.75	0.704	1.315	9.550
	Clay fraction..	33.81	44.91	5.15	5.07	1.31	3.27	.....	0.753	0.872	10.339
	Colloid.....	31.43	41.76	8.93	6.55	1.60	2.84	5.81	0.753	1.006	11.007
Ground rock phosphate...	Original.....	33.73	47.62	5.28	1.78	2.25	3.87	3.03	0.708	1.310	8.716
	Clay fraction..	26.31	36.11	13.64	7.42	4.75	2.49	.....	0.720	1.121	10.506
	Colloid.....	25.02	33.68	14.81	9.03	5.60	2.02	8.19	0.743	1.012	12.386

\* Composed of particles 5 to &lt;5 microns in diameter.

† Without regard to presence of fluorine.

warrant any definite conclusions as to the properties and composition of highly phosphatic natural colloids, the results nevertheless indicate that as regards their physical properties, at least, we may expect to find a decided similarity to the soil colloids which have been studied so extensively and intensively in the Bureau of Chemistry and Soils and elsewhere. The subject promises to be one of considerable interest not only from the academic standpoint but also from the practical standpoint of the phosphate fertilization of crops. In view of this, an extensive investigation of its various phases is planned.

#### ACKNOWLEDGMENT

The authors are indebted to L. T. Alexander of the Soil Chemistry and Physics Division for the mechanical analyses and general mechanical separations, and to D. S. Reynolds of the Fertilizer and Fixed Nitrogen Division for the fluorine determinations given in this paper.

#### SUMMARY

A preliminary investigation has been made of the occurrence of colloidal material in Florida soft phosphate, waste-pond phosphate from the Florida hard rock phosphate district, and Tennessee brown rock phosphate ground to pass a 100-mesh sieve.

Colloidal material amounting to 60.1, 38.6, and 11.5 per cent of the original phosphates was extracted by means of the supercentrifuge from the waste-pond phosphate, soft phosphate, and ground rock phosphate, respectively. In the same order, the colloidal material contained 18.12, 31.43, and 25.02 per cent of phosphoric acid corresponding to 46.4, 38.1, and 8.5 per cent of the phosphoric acid present in the original phosphates.

The indications are that the physical properties of the phosphatic colloids are similar to those of the soil colloids.

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# THE NATURE OF FLOW

BY EUGENE C. BINGHAM AND BAXTER LOWE

WHEN a fluid transpires through a circular tube, the particles of any right cross-section at a given moment will after the lapse of a certain time be found to be in a paraboloid of revolution, hereafter referred to as the flow-surface. This statement is a necessary consequence of the Newton-Poiseuille law, which has obtained its experimental verification from data obtained at varying rates of shear. To be sure, the law has certain limitations and corrections as pointed out by Sir Osborne Reynolds<sup>1</sup> and others.

Of recent years there has been considerable speculation by Green,<sup>2</sup> Buckingham,<sup>3</sup> deWaele,<sup>4</sup> and others in regard to the flow-surface with non-Newtonian liquids and plastic solids. Substances of this type offer the possibility that the flow can be stopped and the flow-surfaces examined, somewhat after the method used by Tresca<sup>5</sup> in his study of the flow of metals.

I. In the Newtonian liquid there has been observed no slippage whatever,<sup>6</sup> and the flow takes place entirely through the shearing of one layer over the other. The velocity at any point in the circular tube is<sup>7</sup>

$$v = \frac{P\phi}{4l} (R^2 - r^2),$$

where  $r$  is the distance of the point from the center of the tube and  $R$  is the radius of the tube. It is observed that the relation of  $v$  to  $r$  is parabolic.

<sup>1</sup> Phil. Trans., London, **174**, 935 (1885).

<sup>2</sup> Am. Soc. Testing Materials, **II**, **20**, 451 (1920).

<sup>3</sup> Am. Soc. Testing Materials, **II**, **21**, 1154 (1921).

<sup>4</sup> Kolloid-Z., **38**, 27 (1926).

<sup>5</sup> Mém. prés. à l'Acad. de l'Institut de France, **18**, 773 (1868); **20**, 75 (1872); **20**, 281 (1872); **20**, 617 (1872); **20**, 829 (1872).

<sup>6</sup> "Fluidity and Plasticity," McGraw-Hill Book Co., 29 *et seq.* (1922).

<sup>7</sup> "Fluidity and Plasticity," McGraw-Hill Book Co., 16 (1922).

II. The second type represents complete slippage at the wall, there being no shearing of the material whatever. The flow-surface remains plane as shown in Fig. 1. The velocity is uniform and equal to the velocity of the material adjacent to the wall  $v = V_R$ . This type of flow does not occur in fluids but it may occur as a limiting case in solids, since it is assumed that the shearing takes place only at a certain threshold value, known as the yield value  $f$ , and this threshold value will be first reached at the wall of the tube, since the shearing stress varies directly as the radius,  $F = \frac{P}{2l} \cdot R$ . If the shearing stress *just* exceeds

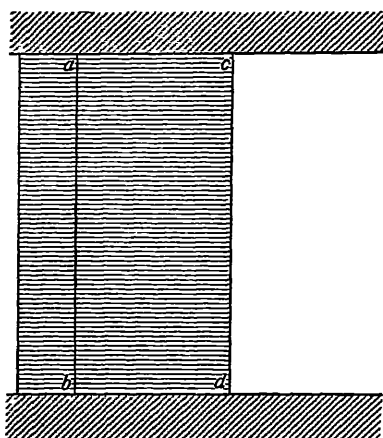


FIG. 1.—Diagram illustrating flow with complete slippage.

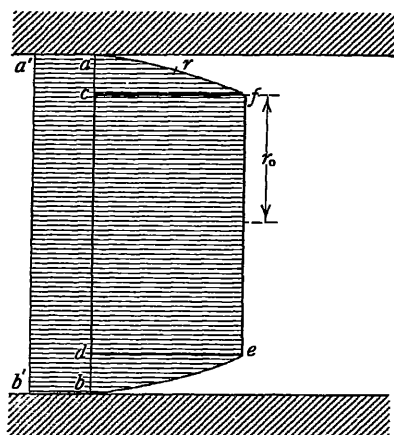


FIG. 2.—Plastic flow, at a moderate rate of flow, showing slippage  $aa'b'b$ , as well as the undeformed core,  $cdef$ .

the yield value, all of the flow will take place in the very thin layer at the wall.

IIa. However, as the pressure is further increased, the shearing stress exceeds the yield value at distances nearer and nearer the center of the tube and the flow-surface will be as shown in Fig. 2, the cylinder  $cdef$  of radius  $r_0$  moving as an undeformed core. The velocity at any point  $r$  is<sup>8</sup>

$$v = \mu \left[ \frac{P}{4l} (R^2 - r^2) - f (R - r) \right]$$

This surface is also a paraboloid of revolution but truncated at the end.

<sup>8</sup> "Fluidity and Plasticity," McGraw-Hill Book Co., 224 (1922).



Iib. As a further case we may assume a certain amount of slippage occurring. The velocity is then

$$v = \left[ \frac{P}{4l} (R^2 - r^2) - f(R - r) \right] + v_R$$

III. No one of these patterns of flow will fit the non-Newtonian liquids in which the apparent fluidity increases as a linear function of the shearing stress, at least as a first approximation,<sup>9</sup>  $\phi_a = \phi_0 + bF$ . The flow-surface at low shearing stresses is a paraboloid of revolution, *i.e.*, the material behaves as a true fluid of low fluidity  $\phi_a = \phi_0$ . As the shearing stress is increased, the apparent fluidity  $\phi_a$  increases, presumably due to a break-down in the structure under higher and higher shearing stresses. The flow-surface is the parabola flattened at the vertex. The non-Newtonian liquid comes to resemble the flow of soft solids of Type II in one respect in that the increase in the flow as the pressure is increased is much more than directly proportional to the pressure. In other words, colloids whether polar or non-polar yield rather suddenly as the stress is applied. This distinction is made clearer by Fig. 3.

In I the apparent fluidity is independent of the shearing stress,  $\phi_a = \phi_0$ . In II the apparent fluidity  $\phi_a \div \frac{8l}{R^4} \cdot \frac{V}{\pi t} \div \left( 1 - \frac{4p}{3P} + \frac{p^4}{3P^4} \right)$ . The two last terms are negligible at very high pressures and thus the apparent fluidity approaches the mobility as a limiting value. The flow reaches a zero value when  $P = p$ , the yield value expressed in terms of pressure.

In polar colloids, on the other hand, the apparent fluidity never reaches a zero value but only  $\phi_0$  as the shearing stress approaches zero according to the formula

$$\phi_a = \phi_0 + bF$$

There is no yield value, but the constant  $b$  defines the rate at which the apparent fluidity increases.

<sup>9</sup> Colloid Symposium Monograph, 5, 219 (1928).

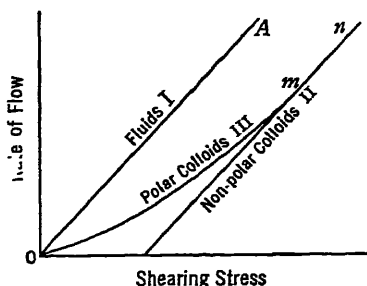


FIG. 3.—Diagram showing the contrast between the three types of flow.

A polar colloid and a non-polar colloid resemble each other at high shearing stresses, when compared over a short range  $mn$ , just as a polar colloid at low shearing stresses resembles a true fluid. At moderate shearing stresses the flow-surface will depart from the paraboloid of revolution, since the apparent fluidity varies with the radius as shown by the formula

$$\phi_a = \phi_0 + \frac{bP}{2l} \cdot r$$

The purpose of our investigation was to find out whether this rather complicated set of predictions would be fulfilled. First a rather stiff

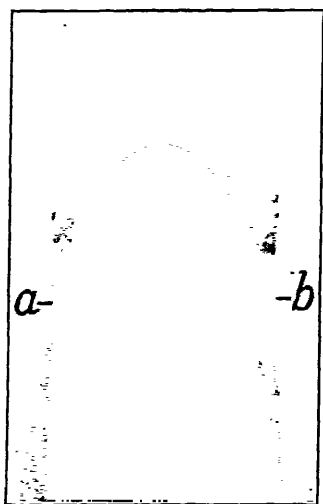


FIG. 4.—A gel made from gelatin, colored originally with lamp-black from  $a$  directly to  $b$ , took the parabolic form as shown with no evidence of slippage, after being subjected to shearing stress for 24 hours. Diameter of tube 2 cm.

gelatin jelly was subjected to shearing stress produced by a constant pressure head of air. The flow-surface was sometimes the free surface but more often a layer of gelatin which was colored by means of lamp-black or dye. By supporting the gelatin in a tube made of nitro-cellulose the tube and contents could be cut lengthwise after the flow had taken place and then photographed. It was found for example that a 5 per cent gelatin in the form of a stiff jelly could readily be made to flow if not enough pressure was used to disrupt it. A single example of the results is shown in Fig. 4, which is quite an exact parabola in the section shown.

A second form of instrument was made by using a metal tube which was split down the middle but held together by clamps. It was fitted with a screw-head at one end to force in the plastic material. A 25 per cent nitrocellulose dispersed in a mixture consisting of camphor, dibutyl-phthalate and alcohol was subjected to flow at different rates. At the rate of 0.033 ml. per second, the flow-surface is a paraboloid but at 5.36 ml. per second the cone is very strongly truncated. Other photographs show intermediate stages as shown in Fig. 5. An increase in concentration of the disperse phase has an effect on the flow surface similar to that obtained by an increase in the rate of flow.

A 64 per cent zinc oxide suspension in mineral oil was used as a type of the non-polar type of colloid. Figure 6 shows nearly complete slippage at the rate of 0.022 ml. per second; at 1.33 ml. per second there is a truncated paraboloid and perhaps slippage. In the case of slippage, the white material very thoroughly cleaned the wall of the tube so that there were very few traces of the black material which had been forced out.

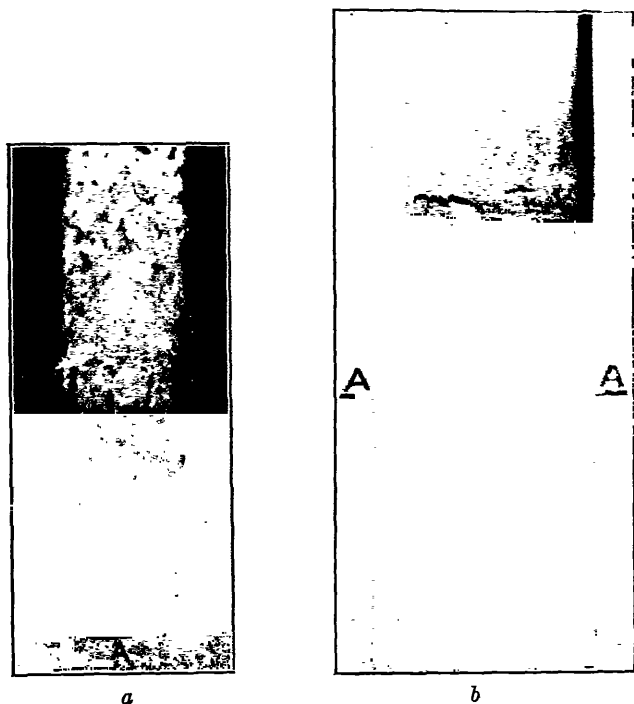


FIG. 5.—The effect of a varying rate of shear in a 26 per cent nitrocellulose dispersion, *a* being sheared at the rate of 0.033 ml. per second and *b* at the rate of 5.36 ml. per second.

These relations apply exclusively to flow through a circular tube, but they do indicate characteristic differences in the materials. It should be noted for example that in cutting a suspension with a thin razor blade, it is necessary to move the blade very slowly in order to obtain slippage and a smooth surface. Rapid movement results in dragging the material. In the polar colloids air-bubbles imprisoned came to the surface in a stiff jelly in a few days, indicating the viscous nature of the material at a low rate of shear.

A few words may be added as to character of the surface due to elastic deformation.

According to the derivation

$$S = \frac{Pe}{4l} (R^2 - r^2),$$

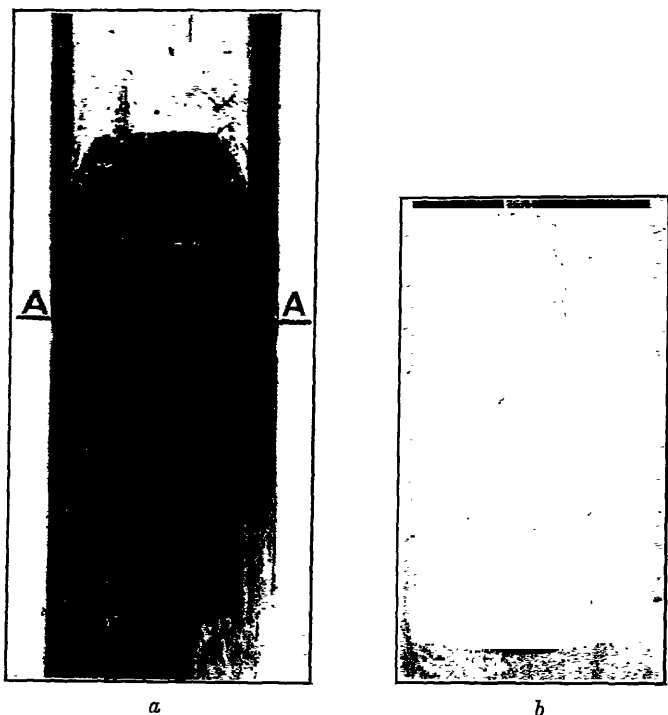


FIG. 6.—The very different effect obtained by varying the rate of shear in a 64 per cent suspension of zinc oxide in mineral oil. There is nearly complete slippage in *a*, which is sheared at the rate of 0.022 ml. per second, but in *b*, sheared at 1.33 ml. per second, the shearing takes place to a considerable distance from the wall.

where  $S$  is the elastic deformation of any point at a distance  $r$  from the center of the tube,  $e$  being the elasticity of the substance. It is to be noted that the deformation surface is a paraboloid.

It is noted that Lord Kelvin<sup>10</sup> conceived of elasticity of shape as being a sure criterion of solids as expressed in the following words: "If a body possesses any degree of elasticity of shape it is a solid; if it possesses no degree of elasticity of shape it is called a fluid."

<sup>10</sup> Article on *Elasticity* in *Encyclopedia Britannica*.

Any failure to obey Hooke's law completely was ascribed by Lord Kelvin to "imperfection of elasticity" rather than to *plastic flow*. This conception was generally accepted; but it was a great handicap to progress to refer to plastic flow as imperfection of elasticity, because the factors which go to make up plastic flow are entirely independent of elasticity. Therefore it is a mistake to make elasticity the criterion of the solid state when as a matter of fact the occurrence of a yield value should be the criterion and the only criterion. This change of view-

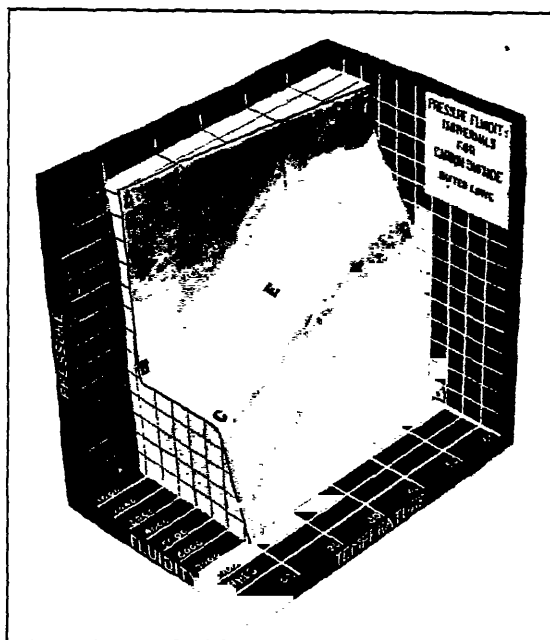


FIG. 7.—The fluidity-temperature-pressure surface for carbon dioxide, from the data of Phillips.

point makes it not only possible to bring many plastic substances under Hooke's law but it also opens the way to the measurement of the elasticity of form in non-Newtonian liquids. There can be little doubt but that some soaps and jellies are elastic and it seems now possible to measure this elasticity.

Finally, it is now possible to express the relation between fluidity, temperature and pressure through the critical state, thus taking in all three states of matter. In Fig. 7 is shown the photograph of a surface showing the fluidity-temperature-pressure relations for carbon dioxide.

There is brought out the nearly linear increase in fluidity as the temperature of a liquid is raised,  $AF$ ; the very slight decrease in fluidity as the pressure in a liquid is raised,  $BA$ ; the slight change in fluidity in gas as the pressure is changed,  $CD$  and  $GH$ ; but the very rapid change near the critical temperature,  $E$ ; and finally the small decrease in the fluidity of a gas as the temperature is raised,  $DH$ .

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# THE ADSORPTION OF FATS FROM VOLATILE SOLVENTS

BY HARRY N. HOLMES AND CLIFFORD J. B. THOR

## I. PROCEDURE

THE biological importance of fats justifies detailed studies of their adsorption behavior.

At first we used liquid fats, dissolved in ether and similar solvents, but we soon found it desirable to use a solid, saturated fat, in order to avoid errors in weight due to oxidation. An "oleo-stearine" melting at 45° C. was used throughout the experiments.

*Adsorption Procedure.*—Adsorption equilibrium was attained by shaking for one hour 20 cc. of the fat solution (weight concentrations of 1, 2, 5, and 10 per cent) with 2 gm. of porous solid adsorbent which had previously been ground to pass through 100-mesh screens and activated at 200–250° C. for 2 hours. The mixture was then filtered through a dry filter paper into a test tube while the funnel was kept covered with a watch glass to check evaporation of the volatile solvent. A known volume of the filtered fat solution was then evaporated to constant weight and the equilibrium concentration determined. Duplicate adsorptions were run for each of these solutions with each of the four adsorbents and two blanks were used for each solution.

Since this work is somewhat preliminary, the evaporation errors are not serious. The general trend of the results is essentially the same as if obtained with an interferometer.

*Solvents.*—The solvents used were ether, acetone, chloroform, carbon tetrachloride, petroleum ether, cyclohexane, benzene, and toluene. These were all dried over anhydrous calcium chloride and filtered immediately before using.

*Adsorbents.*—It was found desirable to use two porous adsorbents:

1. Norit carbon, a commercial vegetable charcoal, was purified by the method of Miller,<sup>1</sup> which reduces the ash content to only a few hundredths of a per cent.

2. Silica gel, prepared by Holmes, Sullivan and Metcalf.<sup>2</sup> This

<sup>1</sup> J. Phys. Chem., **30**, 1031 (1926).

<sup>2</sup> Ind. Eng. Chem., **18**, 386 (1926).

was a fine, white porous powder which had been ground finely enough to pass through a 100-mesh sieve.

3. Hydrated ferric oxide, prepared by adding a slight excess (1214 cc.) of 28 per cent ammonia to 1620 gm. of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  dissolved in 6 liters of water. After standing 50 hours the mixture was filtered through cheesecloth and the gelatinous precipitate was allowed to drain for 5 days. It was then broken into fairly large lumps and kept on drying racks at room temperature for 13 days, the size of the lumps being gradually reduced as drying proceeded. The pieces of gel were now washed with cold and finally hot distilled water during a period of about 8 days until practically free of chlorides. After drying on blotting paper for 4 days the gel was ground to pass a 100-mesh sieve and activated by heating at  $200^\circ \text{C}$ . for 2 hours.

4. Hydrated aluminum oxide, prepared by adding a slight excess (2024 cc.) of 28 per cent ammonia to 2415 gm. of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  dissolved in 6 liters of water. The mixture was allowed to stand 50 hours, filtered and treated in the same way as the iron oxide except that drying on the racks was continued for 16 days. The gel was then washed with tap water and later cold and hot distilled water until almost free of chloride, which required about 15 days. The gelatinous mass was allowed to dry in the air for a day and then in an electric oven kept at about  $60^\circ$  for two days. The dry gel was ground to pass a 100-mesh sieve and activated at  $200\text{--}250^\circ \text{C}$ . for 2 hours.

## II. RESULTS

The percentage of total fat adsorbed from the various solvents by the four solid adsorbents is recorded in Tables 1 to 4. From these tables values of  $\frac{x}{m}$  (grams of fat adsorbed by 1 gm. of adsorbent) and of  $C$  (the equilibrium concentration expressed as grams of fat remaining in 10 cc. of solution) were calculated and plotted, in Figs. 1 to 9, as Freundlich adsorption isotherms.

*Discussion of Results.*—The results show the great influence on adsorption of the relative polarity of all the substances concerned.

Carbon is decidedly non-polar, while silica is polar (and distinctly acidic). Alumina is an amphoteric polar solid, while ferric oxide is basic and polar.

The fat itself is intermediate in polarity, certainly less polar than its own fatty acid, as a comparison of formulas shows.

Of the volatile solvents used ether is somewhat polar and benzene non-polar.



TABLE 1—PER CENT OF ORIGINAL FAT CONTENT ADSORBED FROM 1 PER CENT SOLUTIONS OF OLEO-STEARINE IN VARIOUS VOLATILE SOLVENTS

Solvent	Norit Carbon	Silica Gel	Hydrated Ferric Oxide	Hydrated Aluminum Oxide
Ether.....	49.4	-12.9	- 0.9	3.7
Acetone *.....	85.9	- 3 0	-10.1	- 4.0
Chloroform.....	2.8	15.1	0.2	- 2.3
Carbon tetrachloride.....	31.0	97.8	19.8	70.5
Petroleum ether.....	64.4	98.9	18.3	26.9
Cyclohexane.....	73.4	99.7	23.7	45.1
Benzene.....	12.5	45.3	19.6	35.8
Toluene.....	5.4	48.8	18.9	37.2

\* Saturated solution contained only about 0.6 per cent fat.

TABLE 2—PER CENT OF ORIGINAL FAT CONTENT ADSORBED FROM 2 PER CENT SOLUTIONS OF OLEO-STEARINE IN VARIOUS VOLATILE SOLVENTS

Solvent	Norit Carbon	Silica Gel	Hydrated Ferric Oxide	Hydrated Aluminum Oxide
Ether.....	32.2	-10.1	1.2	3.1
Chloroform.....	0.7	11.1	- 0.1	- 2.1
Carbon tetrachloride.....	18.3	81.7	12.6	41.5
Petroleum ether.....	41.3	97.0	12.7	20.0
Cyclohexane.....	41.8	95.3	13.5	22.9
Benzene.....	8.1	33.2	10.5	19.2
Toluene.....	4.4	36.1	12.5	22.5

TABLE 3—PER CENT OF ORIGINAL FAT CONTENT ADSORBED FROM 5 PER CENT SOLUTIONS OF OLEO-STEARINE IN VARIOUS VOLATILE SOLVENTS

Solvent	Norit Carbon	Silica Gel	Hydrated Ferric Oxide	Hydrated Aluminum Oxide
Ether.....	11.7	- 5.7	3.2	0.7
Chloroform.....	0.0	6.1	- 0.2	- 2.2
Carbon tetrachloride.....	8.7	40.6	6.6	12.6
Petroleum ether.....	17.5	45.8	2.9	9.1
Cyclohexane.....	19.2	49.3	7.0	12.7
Benzene.....	4.2	18.4	4.9	10.4
Toluene.....	2.1	20.1	5.2	10.8

TABLE 4—PER CENT OF ORIGINAL FAT CONTENT ADSORBED FROM 10 PER CENT SOLUTIONS OF OLEO-STEARINE IN VARIOUS VOLATILE SOLVENTS

Solvent	Norit Carbon	Silica Gel	Hydrated Ferric Oxide	Hydrated Aluminum Oxide
Ether.....	4.8	-10.8	-1.1	-2.9
Chloroform.....	-0.4	2.3	-0.5	-1.8
Carbon tetrachloride.....	4.1	21.2	2.5	5.2
Petroleum ether.....	6.8	25.7	1.1	-5.4
Cyclohexane.....	9.3	25.4	2.8	5.2
Benzene.....	1.7	10.7	2.3	4.7
Toluene.....	0.8	11.3	2.4	5.6

The comparison of carbon and silica used with solvents of varying polarity was suggested by the reversal of Traube's rule of carbon adsorption as discovered by Holmes and McKelvey.<sup>3</sup> According to Freundlich's interpretation of Traube's work, carbon adsorbs the higher members of a series of fatty acids better than solutions. Since the higher members of such homologous series are less polar (more like the carbon and less like the polar water), it was predicted by Holmes and McKelvey that the order of adsorption must be reversed when using polar silica to adsorb fatty acids from non-polar toluene. Experiments justified the prediction.

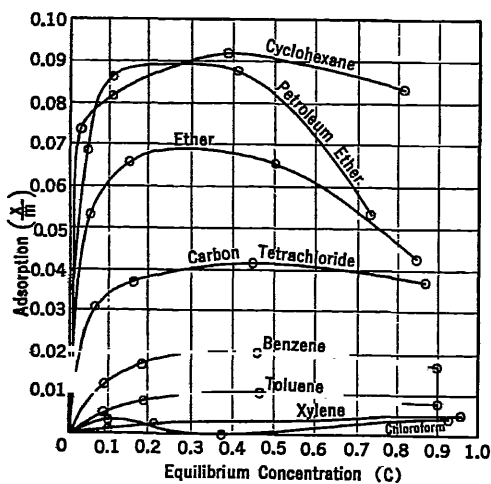


FIG. 1.—Adsorption of a fat from various solvents by carbon (Norit).

<sup>3</sup> J. Phys. Chem., 32, 1522 (1928).

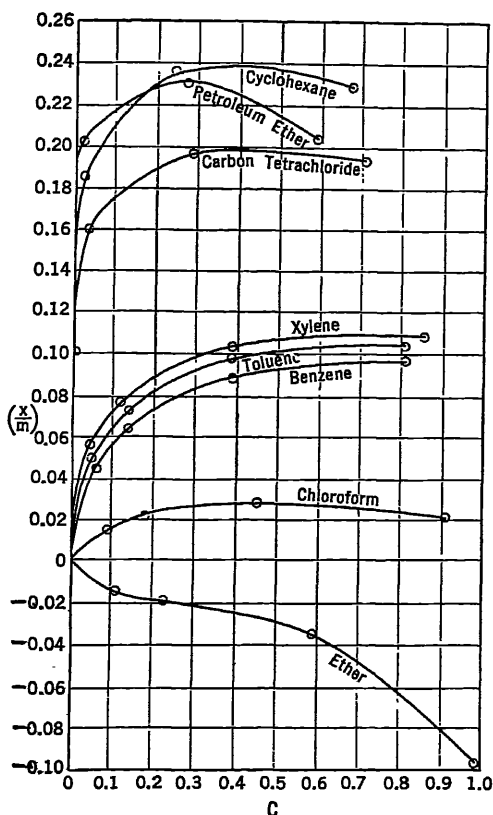


FIG. 2.—Adsorption of a fat from various solvents by silica gel (Holmes type).

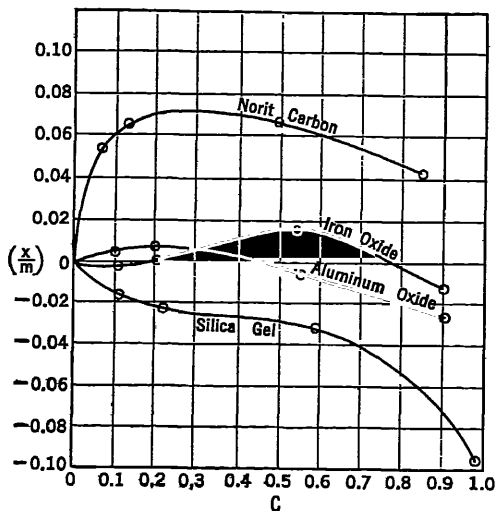


FIG. 3.—Adsorption of a fat from ether by four porous solids.

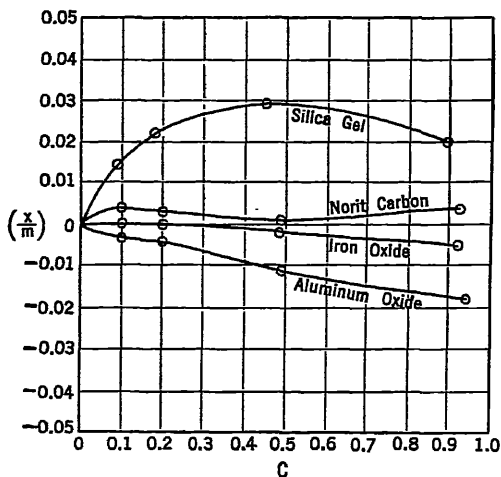


FIG. 4.—Adsorption of a fat from chloroform by four porous solids.

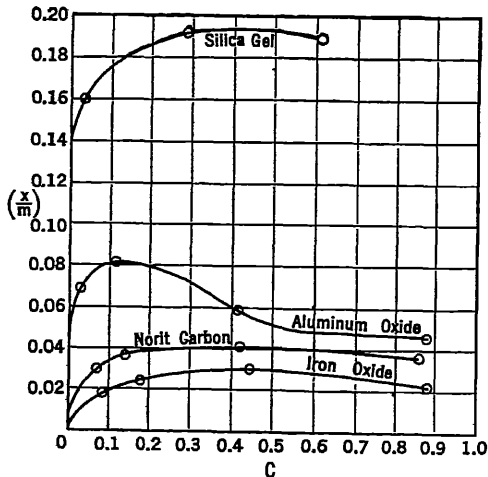


FIG. 5.—Adsorption of a fat from carbon tetrachloride by four porous solids.

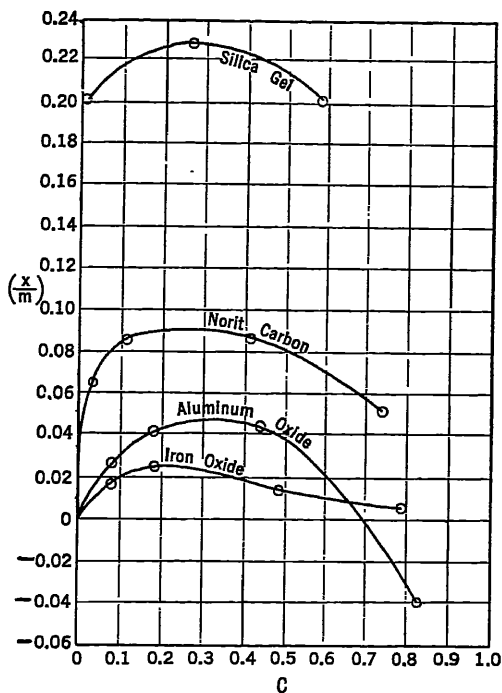


FIG. 6.—Adsorption of a fat from petroleum ether (b.p. 35°-45° C.) by four porous solids.

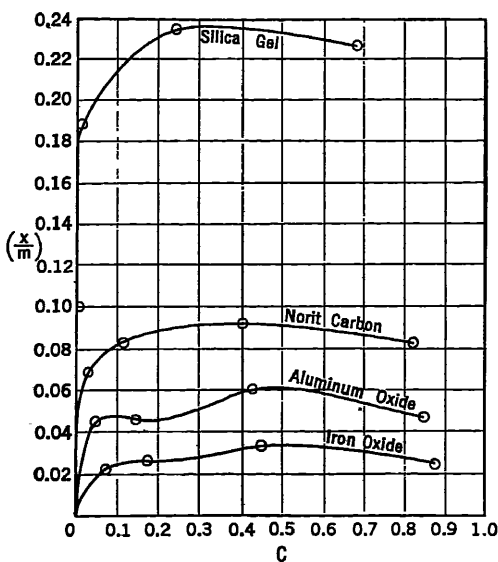


FIG. 7.—Adsorption of a fat from cyclohexane by four porous solids.

THE ADSORPTION OF FATS FROM VOLATILE SOLVENTS

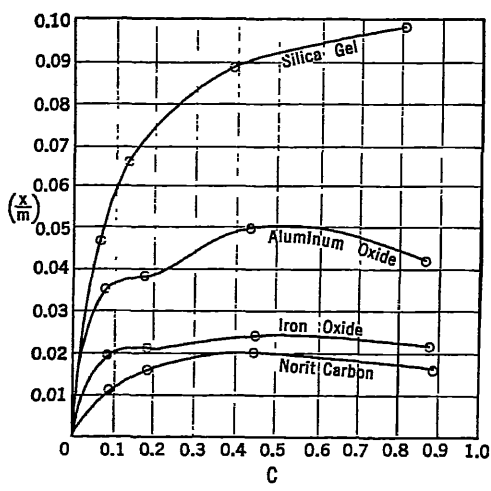


FIG. 8.—Adsorption of a fat from benzene by four porous solids.

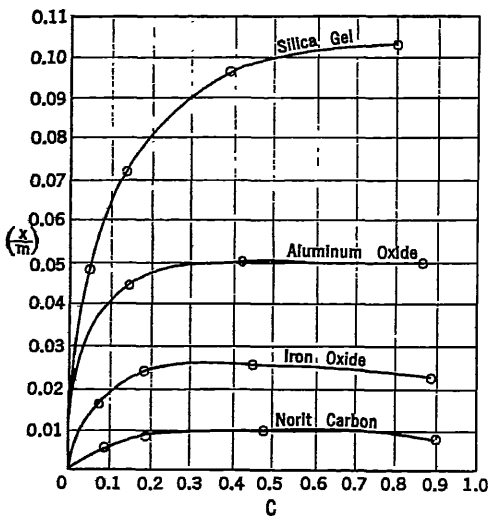


FIG. 9.—Adsorption of a fat from toluene by four porous solids.

So in the present research, the nature of the carbon surface and the silica surface shows differences. Comparing Fig. 1 with Fig. 2 it is seen that the order of adsorption from benzene, toluene and xylene used is reversed. Ether is so polar that it is more adsorbed by polar silica than the fat itself, a result plotted in Fig. 2 as "negative adsorption." Silica adsorbs fat from most of the solvents used three or four times as well as does carbon.

The marked differences in adsorption from the various media cannot be explained by the relative surface tensions of these liquids, since they differ only slightly from each other, as can be seen from the following values:

Solvent	Surface Tension
Ether.....	17.1
Acetone.....	23.7
Chloroform.....	27.1
Carbon tetrachloride.....	26.6
Petroleum ether.....	.....
Cyclohexane.....	25.3
Benzene.....	28.8
Toluene.....	28.4

Knowledge of the interfacial tension between liquid and solid might explain the differences observed, but reliable methods are not as yet available for determining this value.

The solubility of the oleo-stearine in the solvents employed was determined by evaporating 10 cc. portions of the saturated solutions to constant weight. The solubility values obtained were as follows:

Solvent	Grams of Fat in 100 cc. of Saturated Solution
Ether.....	19.9
Acetone.....	0.6
Chloroform.....	46.0
Carbon tetrachloride.....	39.7
Petroleum ether.....	13.5
Cyclohexane.....	25.0
Benzene.....	33.5
Toluene.....	31.6

This shows no consistent relationship between solubility and adsorbability of the fat.

F. E. Bartell (private communication) observes that these adsorption isotherms in general follow the order of adhesion tension as observed by him in studies with carbon, silica and the liquids described here.

Although reliable methods of measuring the total surface per grain of porous solid are not yet at our disposal, it seems that the total surface of the carbon used is of the same order as that of the silica. The oxides of iron and aluminum are much less porous, so comparison with them is not quite fair.

This work is to be continued, and attempts will be made to measure adsorption of various substances dispersed or dissolved in fats in very low concentrations.

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# THE CHEMISTRY OF BACTERIA AND THE DEVELOPMENT OF A PRACTICAL TECHNIQUE FOR THE CHEMICAL ANALYSIS OF CELLS

BY TREAT B. JOHNSON

## I. TREND OF SCIENTIFIC CHEMISTRY

IN his interesting book entitled "Chemical Discovery and Invention in the Twentieth Century,"<sup>1</sup> Sir William A. Tilden, F.R.S., has written in the last chapter as follows: "The future of scientific chemistry will probably depend on the activity of research in two main directions. On the one hand, there will certainly be large additions to the long list of already known definite compounds, especially in the so-called 'organic' division of compounds built up on a foundation of carbon as the characteristic element. In this direction little that is new in principle must be expected. But, on the other hand, developments of physical chemistry will doubtless lead to a better knowledge of the laws which regulate chemical change and which connect together chemical constitution and physical properties. The extension of this kind of knowledge will enable the chemists of the future to calculate in advance what will be the color and crystalline form of any compound it is proposed to make, what its physiological properties will be, and therefore its use, if any, in medicine."

It is the opinion of the author that Professor Tilden has placed too great restriction on the trend of future research activities in organic chemistry, and makes predictions regarding the relationship between organic structure and physical and physiological properties that can hardly be expected to be realized in the near future. He has failed to realize that organic chemists are now treading new paths of adventure, and that several of them together with co-workers, who are developing the field of colloid chemistry, are endowed with a new kind of curiosity that is leading to the successful promotion of research undertakings designed to reveal powers of nature which hitherto have been completely hidden to us. In this future development, under whatever name you may express it, organic synthesis will always play a fundamental part,

<sup>1</sup> Published by E. P. Dutton & Co., New York, 1916.

but this art will not be practiced to exploit further the theory of organic structure by simply building up new organic combinations. While we shall continue to apply the fundamental methods of research which are contributing to our many comforts today, our future progress will undoubtedly be influenced more by the results of cooperative research rather than by those of purely individual accomplishment. The history of chemical science shows that progress has always been made whenever research has been released of restrictions which trammel it, and the writer believes it unsafe to predict what particular trend of scientific activity will have the greatest influence over future progress. We all know that social and industrial advancement has been the result in the past where science has been cultivated and supported. In the practical application of his findings the chemist will still continue to make the world his debtor, regardless of the trend of scientific activity.

## II. CHEMISTRY OF TUBERCULOSIS

The chemical research work on tuberculosis which has been in progress in the Sterling Chemistry Laboratory at Yale University for the past five years represents a new trend of scientific chemistry, which is not dependent for its success on the artificial creation of new organic compounds. The author refers to the extensive and cooperative investigation of this disease which is being supported by the National Tuberculosis Association. Yale's part in this program of cooperative research is confined to the study of a number of fundamental chemical problems dealing with the constitution of tubercle bacilli, which is the cause of this disease, and the coordination of these findings with the results of analyses of other bacterial cells. This investigation is in reality a pioneer undertaking in a special field of experimental science—"chemical bacteriology"—and is more than a mere application of the technique of organic chemistry to the study of cellular organisms. The art of synthesis plays no important part in the program at present. What we are endeavoring to do is to reveal by chemical methods some of the obscure, fundamental chemical changes functioning in the life of a bacterial cell, and if possible to develop practical methods for separating from cells the organic combinations which characterize the biological activity of the respective bacterium.

In other words, an attempt is being made to develop a new and special technique of bacterial analysis which will lead not only to a better understanding of the constitution of tubercle bacilli and bacteria in general, but also to making available for experimental studies by biologists and clinicians definite and specific cell fractions which hitherto

have not been obtainable. The newer problems dealing with the phenomena of immunity, of symbiosis, cell synthesis, cell assimilation, toxin and antitoxin: formation, germicidal action, and anesthesia are dependent for their correct interpretation on a more exact knowledge of the chemistry of the life processes of the growing cell. We are dealing in this work with an aspect of scientific chemistry that is fundamental in nature and having biological significance, and which coordinates with other research activities organized to reveal scientific truths which can be applied for the improvement of man's physical development.

This cooperative research activity is an excellent illustration of the practicability and productivity of the present-day plan of carrying on research in related fields of science. It is now generally realized that the greatest progress in the solution of broad research problems is made through a joint and coordinated attack by a group of investigators trained in their respective fields of science. Our research on tuberculosis represents one of the newer trends of scientific chemistry and does not depend for its final success on the accomplishments of any one group of specialists.

### III. CHEMISTRY OF CELL PROCESSES

Most of the efforts of the organic chemists in the past, or since organic chemistry became a science, have been concerned with an intensive study of animal and plant degradation products representing thousands of years of geological time. We have been studying the end products of a complicated series of chemical process of which we have no accurate early record. In our chemical investigations we have applied a technique involving a continuation of this degradation process by artificial means. Coal and petroleum have been the major natural resources to which we have applied this crude technique. We have given a wonderful demonstration of the utility of our science and have learned the comforts to be derived from the many products which have been obtained from these natural resources, but we have failed to demonstrate the hidden powers of nature, and to reveal the mechanisms of the primitive processes of life changes. It is now acknowledged that a better understanding of the primary reactions of early life processes is very important, and the chemist has finally realized that he has at his command a technique which can be applied with success for the acquisition of this new knowledge. In undertaking the study of these newer problems embraced under the term "Chemical Bacteriology" the chemist is pioneering, therefore, in an entirely new field which promises to surpass in chemical interest any one that we have cultivated previously.

One cannot enumerate in a paper of this length the many problems which are presented for solution when one tries to evaluate the scope of bacterial chemistry. The complicated phenomena of catalysis as applied to cell growth are probably the most important biologically. The phenomena exhibited, for example, by enzymes, and the potent organic secretions of the ductless glands, cannot fail to excite wonder at the remarkable activity of these sensitive and complex organic substances. In the near future we shall be concerned in ascertaining to what an extent all the natural processes of absorption, assimilation, growth and general development of cells are dependent on forces which are entirely catalytic, or whether we are dealing with complex chemical changes which are brought about through the agency of living protoplasm in the cell. The author fails to understand how any organic chemist can decline to become interested in the synthetic operations which we see being effected in cells through the agency of complex mixtures of nitrogenous substances contained in the protoplasm, and which are themselves at the same time constantly in process of formation and decomposition. We have to deal also, in the study of life processes, with secondary changes leading to the formation of by-products which in many cases probably represent the most important metabolic products appropriated for our practical service. When allowed to accumulate in the cell these may act as toxins and actually obstruct the normal process of growth. It is possible that certain of these by-products—vitamine substances—may prove to be the most important units influencing normal growth and development, and it behooves the chemist to isolate and study all such compounds which can be detected as a result of his analysis. It is necessary to differentiate between organic combinations which are merely waste products and those which serve as essentials to normal growth. Our study of bacteria has introduced us to many of these interesting problems and we have learned by experience that their investigation cannot be undertaken successfully without a full cooperation of voluntary agencies, and the sponsorship of researchers representing various open-minded groups.

#### IV. CELL ENVIRONMENT

When we began our researches on the "Chemistry of Bacteria" we were able to find very little in the literature which was of help to us in organizing a chemical basis of attack. The knowledge of the chemistry of microorganisms was very fragmentary, and is even today far from exact. Previous workers in this field had generally operated without any organized procedure or system and consequently had contributed

very little which we could appropriate as an aid in developing a precise plan of chemical investigation.

One of the most important factors that we had to consider before organizing any procedure of reliable analysis of bacteria was the influence of environment on cell growth. It is a well-known fact that bacteria are affected by their chemical environment. Growth, death, physiological characteristics, pathogenesis and morphology are all very susceptible to chemical and physical influences. Furthermore, bacteria have the ability to produce marked changes in their environment and in some cases with a rapidity that is marvelous. Chemical products are formed either as a result of synthesis within the cell, or of autolytic changes which are generally attributed to enzymes normally produced within the cell. All of these phenomena are dependent on orderly and related chemical transformations calling for an accurate knowledge of the chemical composition of cells and the constituent parts of cell structure. For the proper and accurate study of bacterial composition it was important, therefore, to have our microorganisms grown and cultivated under standard and uniform conditions on synthetic media of known composition; otherwise it would be impossible to make reliable quantitative comparisons of the results of cellular analyses of different bacteria. In other words, it was necessary to coordinate our program with that of the bacteriologist and jointly to instruct the manufacturer regarding the proper conditions for gross production.

## V. COMMERCIAL PRODUCTION OF BACTERIA

In consequence of these facts it has been necessary for us to pay considerable attention in the first stages of our research to the problem of gross production of living bacteria. Not only was it necessary for us to consider the changes influenced by environment during growth, but it was also necessary to operate on an industrial scale that would be productive of bacteria in any quantity needed for successful chemical research. The cells of bacteria are so minute that any study of their composition must be carried out with masses of cells. The chemical study of single isolated cells is impossible. Such a resource had never been provided to chemists, with the single exception of yeast cultivation, before we instituted our new program of research on tubercle bacilli.

Fortunately, we have had the cordial cooperation of competent industrial organizations<sup>2</sup> in the production of microorganisms for our work, and now bacteria of several types are being grown on synthetic

<sup>2</sup> Mulford & Co., Glenolden, Pennsylvania; Parke, Davis & Co., Detroit, Michigan.

media in quantities far beyond the requirements or capacity of our present research organization. We are hoping that other workers will become interested in the chemistry of bacteria and will cooperate with us in extending our knowledge of a field of biochemistry which concerns the welfare of every human being. Thus far, we have neglected the problems calling for the application of the principles of colloid chemistry. The lack of this cooperation has been a source of regret many times in the course of our researches. We feel that a well-trained colloid chemist would find many interesting problems opened up to him for investigation if he became interested in the study of bacteria and the physical conditions affecting their growth. A standard synthetic medium has been devised by Professor Long of the University of Chicago which has fulfilled completely all the nutrient requirements for the successful growth of tubercle bacilli and the different bacterial organisms thus far incorporated in our investigations. It is very probable, however, that we shall need to change the composition of this for the successful growth of some of the organisms needed for our future work.

Being endowed with a short life-cycle, naturally the growth of bacteria in some cases is very rapid; a fact which connotes a speedy production of the characteristic products of cell metabolism. If any measurements of these metabolic substances are to be used for making any quantitative comparisons between different cellular organisms it is, of course, very necessary that accurate methods must be available for determining the extent of these characteristic changes. The development of a practical technique applicable for cell analysis, however, involves many difficulties that were not anticipated when we began our investigations, and our preliminary accomplishments have simply been limited to the laying of a foundation on which to build an analytical procedure for future use. The relationships between growth and metabolic change are not simple, and in the opinion of the author there is not sufficient evidence to warrant drawing the conclusion that there is a direct proportion between the growth of a cell and the amount of any one product of metabolism. In addition to this, we do not have an accurate understanding at the present time of the different stages of development characterizing the life-cycle of any bacterial organism. Consequently we have difficulty in differentiating between chemical changes produced during the normal life-cycle of the cell, and those brought about by the agency of enzymes or through autolysis after the cessation of growth or death of the cells. Due to the complexity of the different stages of growth we cannot at the present time tie up to any specific analytical determinations or tests which makes it possible to characterize these different stages. The best that we can propose at

present is to be certain that all cells be typical of the type or species under examination and that they be free from all foreign material. This demands careful control of the absorption of materials in the medium, and the prevention of losses of easily diffusible cell constituents in washing operations and in technique calling for the application of dialysis. In all these analytical operations one constantly encounters conditions calling for a knowledge of the colloidal behavior of organic materials of the nature of proteins, lipoids, etc.

## VI. MACRO-CHEMICAL ANALYSIS

In our research program to date we have been concerned entirely with the determination of cell composition by means of methods applicable for gross chemical analysis. We have not used in our work micro-chemical or tinctorial methods, depending on such technique only for purposes of identification of unknown fractions produced in very small quantities. The macroscopic methods have proved quite sufficient to date as our major problem has been one calling for proximate analysis only, and the separation of specific unit fractions from large quantities of bacterial cells. This has seemed to be the most practical procedure for coordinating the chemical, biological, and clinical work of our cooperate research and the finer analytical technique is applied to those fractions which reveal themselves as potent substances after preliminary biological tests of gross fractions.

The cell constituents receiving first attention have been the following: proteins, nucleic acids, carbohydrates, lipoids, and waxes. It has been important to determine the relative proportions of the major organic fractions in order to obtain information regarding the variations in composition of cells of different types. Textbooks in bacteriology tell us that the composition of bacterial cells agrees with that of other forms of life in so far as the building stones of proteins, nucleins, phosphatides, stearols, lipins and sugars are known. This statement, however, is based on very limited experimental evidence, and the results of our preliminary work already indicate that very fundamental structural differences exist in cells of different types which hitherto had not been realized.

Microscopic examination of bacteria shows that the protoplasm of their cells is not homogeneous. When one considers that they contain about 70 to 80 per cent by weight of water, and as colloidal bodies, show large powers of adsorption, it is at once apparent that cells can readily adapt their composition to that of the media in which they are grown. As a result every fundamental constituent group of the cell can be affected quantitatively. The composition is also governed by the age

of the cells, old cells undergoing profound autolytic changes which have a special significance. All of these factors have to be taken into consideration in planning any technique of gross analysis, and our estimations are bound to be more or less inexact from a purely quantitative point of view. In many of our operations involving extraction by different solvents it is known that we are dealing with colloidal states, and in the case of our protein extracts it is questionable whether we are ever dealing with true solutions. In consequence of these physical conditions many difficulties are encountered in our purification processes, and losses take place which cannot be avoided with present methods of technique. The high speed centrifuge has given an invaluable service in our large scale operations. Improvements in the technique of dialysis have also been of great service in this work.

## VII. CHEMICAL COMPOSITION OF CELLS

The fundamental groups which are included in our scheme of cell subdivision for further analysis are represented as follows:

I. *The Lipoid and Wax Fraction.*—This is the fraction extracted by organic solvents and constitutes a very large proportion of some bacterial cells, especially the acid fast group. This fraction has recently been shown to be one of the most important groups biologically of the tubercle bacilli cell. Dr. Anderson of the Yale Laboratory has succeeded in separating from the phosphatide fraction of the lipid unit an optically active fatty acid which is very potent biologically. It occurs, however, in very small amounts only and consequently large quantities of cells are required for its production.

Doctors Sabin and Doan of the Rockefeller Institute have shown that this bacterial acid has the power to stimulate the development of normal tubercle cells when injected into the body of the rabbit. The structure of these biologically active acids has not been determined, and before we shall be able to submit them to an extensive chemical investigation it will be necessary to operate with larger quantities of cells than have hitherto been available in consequence of the low yield of the potent material. The lipid fractions of the three types of tubercle bacilli—human, avian and bovine—have received more attention thus far in our laboratory than any other group of cell constituents, and from each type of tubercle bacilli specific fatty acids of high potency have been isolated.

II. *The Nucleic Acid Fraction.*—This represents only a very small proportion of the whole cell, and according to our preliminary analyses corresponds in its composition very closely to that of the nucleic acid



present in the thymus gland. It is apparently a nucleic acid of animal origin containing the two pyrimidines, cytosine and thymine. We have also obtained evidence that methyl-cytosine is a constituent of this acid. It will be important to compare the nucleic acids from different bacteria in order to determine whether they are similarly constituted. At present we have practically no knowledge of the biological activity of these nuclear compounds.

III. *The Cell Proteins*.—We subdivide these into three unit fractions as follows: water soluble protein, alkali soluble protein, and sclero-protein. The water soluble protein of the tubercle bacilli cell exhibits all the physiological properties of the active tuberculin protein which is contained in the synthetic culture medium of this organism. This fraction is very probably a mixture of different proteins and it is very susceptible to chemical change. Its biological activity is lowered and gradually lost by prolonged treatment with alkalis.

The alkali-soluble protein fraction represents a considerable part of the bacterial cell. This also is undoubtedly a mixture of protein substances, and at the present time we have no evidence that it is characterized by any special biological activity. The protein fraction of the cell remaining after removal of these soluble groups is classified as sclero-protein, and represents the largest single unit of the cell structure. Regarding its composition we have no accurate knowledge. It gives a strong biuret test characteristic of protein and after hydrolysis with acids yield a large proportion of reducing sugars and also a considerable quantity of fatty material.

IV. *The Polysaccharide or Sugar Fraction*.—Different combinations of this group of compounds are found distributed throughout all the different fractional groups of the cell with which we have worked. Sugars are found uncombined in both the medium and water extracts of the cell. They are also conjugated with proteins, combined in nucleic acids and linked in combinations found in the lipid fraction. Apparently both pentose and hexose constructions are present. These sugar combinations undoubtedly represent one of the most important major groups constituting the tubercle bacilli cell. The study of their constitution is now in progress in our laboratory. We have already obtained experimental evidence indicating that the carbohydrates from different types of bacteria differ in molecular constitution, and it is our belief that they play a very significant part during cell growth, and influence the specificity of the respective bacterial organism.

V. *Non-protein Nitrogen*.—In this group are included a number of unknown products of cell metabolism which distribute themselves through all the fractions when extractive methods are applied. Thus

far, we have had no time to pay any attention to these substances. Organic combinations of simple structure are undoubtedly represented here which play important parts in the processes of cell growth. Their chemical investigation will be taken up after some of the more important features of cell composition have been investigated.

In conclusion the author desires to emphasize the preliminary nature of our investigations to date. We have initiated a research development which can be applied to any form of bacterial organisms. Whether our analytical procedure will permit of differentiations between bacterial forms remains to be decided. We believe, however, that through the cooperation of our biological workers we shall finally arrive at important conclusions which will make possible important differentiations, new generalizations and important comparisons.<sup>3</sup>

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\* A list of our publications on "Chemistry of Bacteria" up to the end of 1928 is recorded in the following paper: *Am. Rev. Tuberculosis*, 18, 505 (1928).

# HUMAN BLOOD SERUM AS A COLLOIDAL SYSTEM

BY S. DEW. LUDLUM, A. E. TAFT, AND R. L. NUGENT

IF a drop of blood is taken from the finger before breakfast and examined with the dark-field microscope, the appearance is as shown in Fig. 1. The two large bright objects are white corpuscles and the smaller more circular ones are red corpuscles. The latter average about  $7-8\mu$  in diameter. Each cubic millimeter of human blood contains, on the average, about eight thousand of the whites and an astounding number, five to six millions, of the reds. The particular point to be noted here is that in this fasting specimen, the solution in which the cells float, the blood plasma, is quite free from bright particles.

If another drop is taken from the same person a few hours after breakfast, and similarly examined, the plasma literally teems with bright particles as shown in Fig. 2. Unfortunately this static representation gives but a poor idea of the true picture, as the particles dance hither and yon and in and out of focus in rapid and brilliant Brownian motion. Edmunds,<sup>1</sup> in 1877, remarked that blood under the dark-field microscope seems like a wholly new substance with multitudes of dancing particles which look like motes in a sunbeam. Because of this appearance they are sometimes called the "blood dust."<sup>2</sup> Gage and Fish<sup>3</sup> in a classical study of these particles have called them chylomicrons, because they enter the blood with the chyle, a solution containing absorbed food from the intestine which pours directly into the blood stream. Briefly, the blood can distribute all the food materials in true solution with the exception of the fats; so, with masterly choice of materials and colloid technique, it does the logical thing, and distributes them as this fine emulsion of chylomicrons, estimated to be mostly from  $0.5$  to  $1.0\mu$  in diameter.

After a meal including fats the number of chylomicrons in the blood increases for several hours and then decreases to the fasting level, practically zero. The time factors are such that this fasting level is reached over night, which accounts for the clear plasma in Fig. 1. Analytical

<sup>1</sup> Monthly Micr. J., 18, 78 (1877).

<sup>2</sup> Bayliss: "Principles of General Physiology," 375 (1927).

<sup>3</sup> Gage and Fish: Am. J. Anatomy, 34, 1 (1924).

## HUMAN BLOOD SERUM AS A COLLOIDAL SYSTEM

show that the fat content of the plasma follows the same general pattern that is, there is a rise after meals followed by a fall to the fasting

When blood clots, a jelly-like mass is formed which contains all the solid elements and some of the proteins and electrolytes from the blood. The remaining solution is called the blood serum. It has been

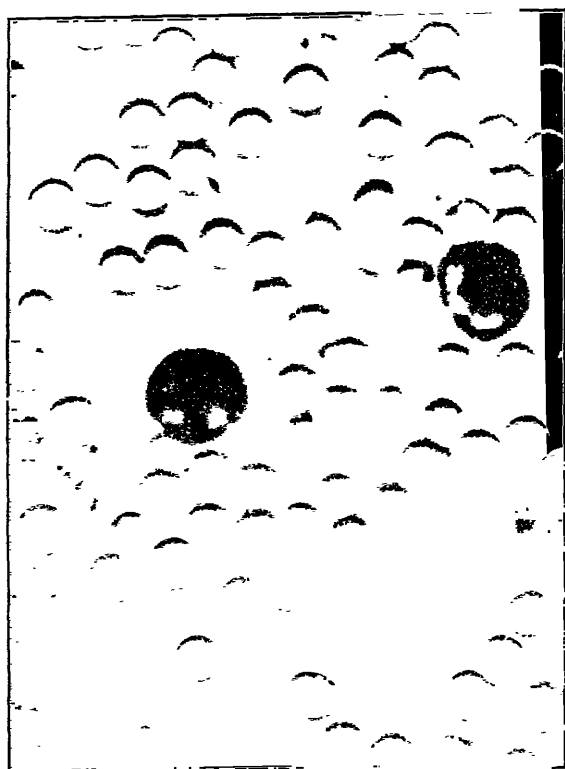


FIG. 1.

effect of an untold number of investigations, because it is simply fundamental and, although differing from the plasma of the living animal, has a known relation to it. Human blood serum is a solution composed principally of about 90 per cent water, 7.5 per cent protein, 0.5 per cent salts, 0.15 per cent dextrose plus urea and a few tenths of a per cent of lipoids including fats, lecithin (phosphatides) and cholesterol. It is separated from a blood taken before breakfast and examined by Landsteiner and Heckscher: *Biochem. Z.*, 149, 83 (1924).

under dark-field conditions, few particles are to be seen; but serum blood taken a few hours after breakfast appears as shown in Fig. 2. The separation of the clot leaves the chylomicrons in the serum supernatant. The important thing here, from the point of blood serum as a colloidal system, is that it is not only a protein solution as generally considered, but under ordinary conditions is also a lipid emulsion and therefore a veritable mine of colloid interest.

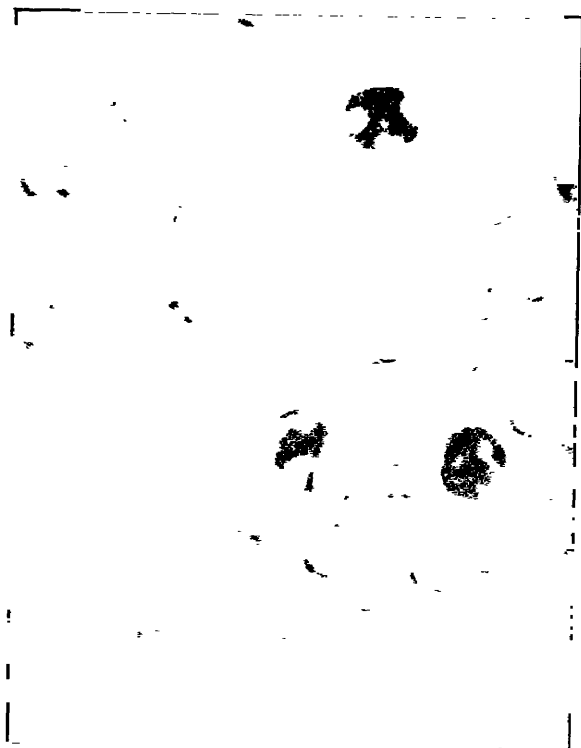


FIG. 2.

transport of fats in fine droplets is well recognized,<sup>5</sup> and since the work of Gage<sup>6</sup> there has been considerable interest in the matter of using chylomicron count as an index of fat content.<sup>7, 8, 9</sup> The opinion is held to be that there is definitely a relation between the two and that

Am. J. Physiol. Rev., 2, 92 (1922).

Cornell Veterinarian, 10, 154 (1920).

Howard: J. Biol. Chem., 55, 357 (1923).

Johnson and Grigg: Proc. Soc. Exptl. Biol. and Med., 20, (8) 462 (1923).

or, Gillette and James: J. Biol. Chem., 75, 61 (1927).

the count is a valuable adjunct to blood and serum fat determinations.

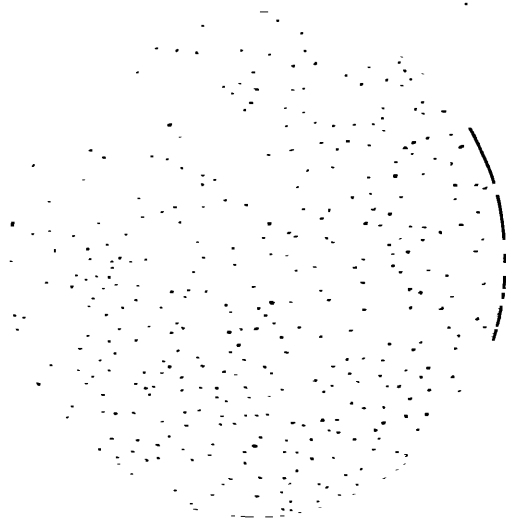


FIG. 3.

The question of the comparison of the chylomicron count and the lipid content is also important in the consideration of the chylomicrons as the disperse phase of an emulsion. If they are lipoidal in nature and are of more or less uniform size, and if they can be counted with some accuracy, there must be some sort of linear relation between the counts and the lipid contents. If not, the departure from this relation should be

interpretable in some way to increase our knowledge of the transport of lipoids by the blood.

Eight sera were chosen from different individuals in such a way as to cover the normal daily range of chylomicron counts. The lowest was in a serum taken after an over-night fast and the highest from one taken near the height of the absorption after an ordinary meal. The counts were made by the method used by Gage and Fish,<sup>10</sup> and the ether-soluble contents were determined as the measure of the lipid content. The method for the latter was that of Gettler and Baker,<sup>11</sup> being in principle

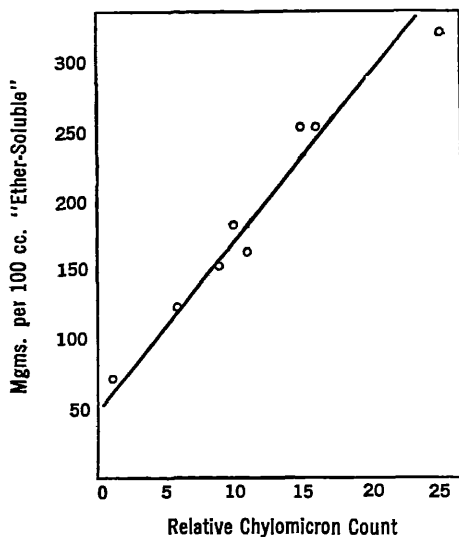


FIG. 4.

<sup>10</sup> Gage and Fish: *Am. J. Anatomy*, **34**, 1 (1924).

<sup>11</sup> *J. Biol. Chem.*, **25**, 218 (1916).

the extraction of thoroughly dried samples with anhydrous ether. The results are shown in Fig. 4 and demonstrate quite a striking linear relationship. The values obtained are in satisfactory agreement with those of Gettler and Baker<sup>12</sup> and of Bing and Heckscher<sup>13</sup> who also used anhydrous ether. The latter state that this solvent extracts free fat to the practical exclusion of lecithin and cholesterol.

It should be remembered that the best estimation of the size of the particles has them varying from 0.5 to 1.0 $\mu$  in diameter, that is, eight-fold in volume. These estimates are admittedly inaccurate as is the counting of particles in rapid Brownian motion. The regularity found is thus much better than might be expected and is evidence either of greater uniformity of size than the estimates would indicate, or a uniformity of size distribution as between individuals. It indicates the possibility of the application of the chylomicron count as an independent method for the estimation of the fat content of sera, at least under ordinary conditions.

The chylomicron emulsion is the most important emulsion in existence. Even milk must take second place. It is therefore strange that the writers have been able to find not only no record of investigations directed toward the determination of the stability factors involved, but even no discussion of their possible nature and importance. The colloid chemistry of the chylomicrons is thus a neglected field.

The major serum lipoids, fats, lecithin, and cholesterol, are present in about equal amounts of the order of 100-250 milligrams each in 100 cc. of fasting serum. It is a most interesting fact, that while lecithin promotes oil-in-water emulsions, cholesterol promotes those of the water-in-oil type. Seifriz<sup>14</sup> emulsified olive oil in water using lecithin as the emulsifying agent and water in olive oil using cholesterol. Corran and Lewis<sup>15</sup> later found a definite antagonism between the two. Starting with lecithin dissolved in water and cholesterol dissolved in olive oil, they found the inversion point to be in the neighborhood of a lecithin-cholesterol ratio of one to one. This is a most striking result because the lecithin-cholesterol ratio in serum has just about this same value. It is suggestive of a rather finely drawn physiological balance. Be that as it may, the possibility remains that lecithin may be important as an emulsifying agent in determining the stability of the chylomicron emulsion. It is also possible that serum protein is an important agent since, for

<sup>12</sup> J. Biol. Chem., **25**, 218 (1916).

<sup>13</sup> Biochem. Z., **149**, 83 (1924).

<sup>14</sup> Am. J. Physiol., **66**, 124 (1923).

<sup>15</sup> Biochem. J., **18**, 1364 (1924).

example, Seifriz<sup>16</sup> emulsified olive oil in water with serum albumin just as well as with lecithin.

When an emulsifying agent covers the surface of disperse emulsion droplets, they necessarily show the surface behavior characteristic of the agent. A pure lecithin sol shows the greatest tendency to aggregate at pH 2.3.<sup>17</sup> If albumin is added to the solution, this value changes to 4.7, the isoelectric point of albumin, and if globulin is added it changes to 5.3 which is close to the isoelectric point of globulin. This not only illustrates the point but is directly applicable to the question. Thus it seems that even though lecithin concentrated in the chylomicron-serum interface, serum protein would in turn concentrate in the resulting lecithin-serum interface, and the surface properties of the chylomicrons would be those of protein. It would be a case of what Alexander<sup>18</sup> has called cumulative protection, that is, the first protective agent in turn protected by a second.

Fortunately everything pointed to the same type of experiment. The pH of serum is about 7.4. By gradually increasing the acidity, the

isoelectric regions of the different serum proteins would be reached and passed as would the region of greatest aggregation tendency of lecithin sols, assuming the latter to be unchanged by the presence of the serum salts. Portions of serum containing chylomicrons were accordingly mixed with equal volumes of hydrochloric acids varying in strength from N/16,000 to 4N. In any series the strength of each acid was twice that of the next weaker

FIG. 5.

one. A drop of each mixture was placed on a slide under a coverslip sealed with vaseline, and examined with the dark-field microscope after standing for ten minutes. With strengths from

<sup>16</sup> Am. J. Physiol., 66, 124 (1923).

<sup>17</sup> Höber: "Physikalische Chemie der Zelle und der Gewebe," 752 (1926).

<sup>18</sup> "Colloid Chemistry," 1, 625 (1926).



N/16,000 to about N/100 the appearance was such as shown in Fig. 3.

No change could be observed as compared with an original serum of the same chylomicron count. However, in the range from N/100 to N/30 a gradual and most striking phenomenon appears, one stage of which is illustrated in Fig. 5. Aggregations of the chylomicrons appear accompanied by a regular decrease in the number of single particles. With about N/30 acid practically no free particles remain, as shown in Fig. 6. In the

range from N/30 to N/4 acid there is again a region in which the chylomicrons seem almost completely dispersed.

FIG. 6.

From N/4 to normal acid there is a second zone of aggregation, this time of a somewhat different type, the aggregated particles seeming larger and brighter than before, and large individual refractile globules tend to appear on longer standing. There are numerous cases where aggregates can be observed clinging to such globules. This state of affairs is illustrated in Fig. 7. With 2N and 4N acids copious precipitation of protein occurs and a complete

FIG. 7.

cracking of the emulsion tends to take place, the aggregates tending

to run together to form a relatively small number of large refractile drops. Fig. 8 shows one such drop in the protein mass.

The first zone of aggregation followed by one of dispersion is presumably the isoelectric zone of the chylomicrons which is in turn



Fig. 8.

presumably the isoelectric zone of their external emulsifying agent. The pH of a mixture in this zone was determined and found to be 4.7,<sup>19</sup> in the range of the isoelectric points of the serum proteins, and thus sup-

<sup>19</sup> Ludlum and Taft: Alexander's "Colloid Chemistry," 2, 695 (1928).

porting the prediction that the chylomicrons are stabilized by protein films. An average  $pH$  of 5.1 was found in a series of 15 further determinations. A similar condition exists in milk where it has long been believed that the fat globules have protein films around them.<sup>20</sup> Recent work indicates this protein to be ordinary casein.<sup>20</sup> A great many years ago it was observed that it was most difficult to extract the fat from ordinary milk, with ether, but that when sufficient acid had been added to destroy the protein films the extraction was easy.<sup>20</sup>

The remarks as to milk lead up to the interpretation of the rest of the observations. The second aggregation into larger brighter particles with the appearance of large individual globules and, finally, the tendency toward the complete cracking of the emulsion occurs when the acid is sufficiently strong to weaken the protein films and finally destroy them. It is probably a matter of progressive dehydration. This point of view is borne out by the facts that the phenomenon first appears with acids just weaker than the one which first causes copious protein precipitation, and is most pronounced with the latter. They also support the basic view that the chylomicrons are protected by protein films.

Figure 8 is a photomicrograph. Figures 3 and 5 to 7 are artist's drawings. It seemed very difficult to get good photographs of the chylomicrons and their aggregations because of Brownian motion and difficulties in focusing. Several unsuccessful attempts were made to get motion pictures of the former. Figure 9 is an example of the sort of photograph obtained of the second type of aggregation.

Even at this preliminary stage in the investigation of the colloid chemistry of the chylomicrons, a most interesting possible application in medicine appears. In precipitation tests for the detection of syphilitic sera,<sup>21</sup> an alcoholic extract of heart muscle is mixed with a salt solution. The extract contains lipid material from the muscle which is precipitated in the form of a suspension. On further mixing with a syphilitic serum, aggregations of the suspended lipid particles are formed whereas with normal sera this is not the case. These precipitation tests are sometimes called "lipoid fixation" tests. Figure 10 is a representation of the microscopic appearance of such lipid aggregates. There is a marked similarity in appearance between them and the lipid (chylomicron) aggregates which have just been discussed as occurring in acidified sera. The striking thing is that the acidification of syphilitic sera is known to make them more sensitive to the lipid fixation tests,<sup>22</sup>

<sup>20</sup> Titus, Sommer and Hart: *J. Biol. Chem.*, **76**, 237 (1928).

<sup>21</sup> Kahn: Alexander's "Colloid Chemistry," **2**, 757 (1928).

<sup>22</sup> Kahn: *Loc. cit.*

and that even normal sera give a positive result when the concentration is about 0.03 N with respect to hydrochloric acid.

Normal serum appears to stabilize the suspended lipid droplets of the so-called antigen emulsion, whereas syphilitic sera lead to their

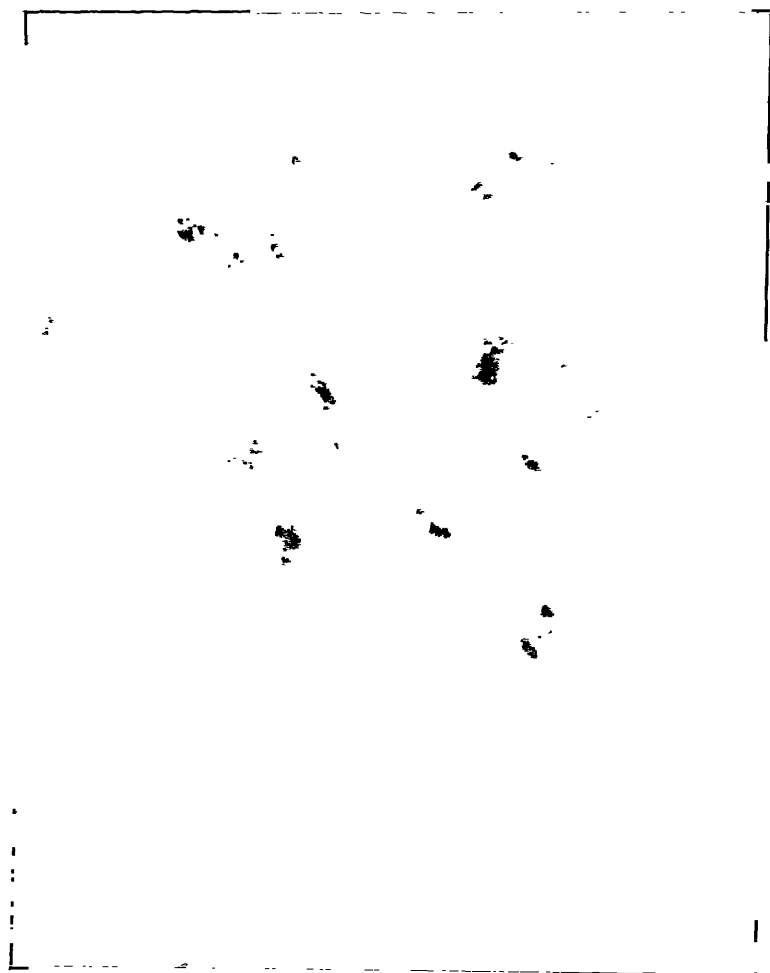


FIG. 9.

aggregation. Acidification increases the tendency toward aggregation in all cases. It has been shown here that acidification to about the same extent also increases the tendency toward aggregation of the chylomicrons, which are apparently stabilized by protein films. It is thus possible

that the difference between syphilitic and normal sera leading to their differentiation by means of precipitation tests rests in the character of the protein film formed around the droplets of antigen suspension when the suspension is added to the serum. In any case the aggregation of the chylomicrons is a "lipoid fixation" phenomenon in normal serum without the addition of antigen, which is sufficiently unorthodox to be interesting.

The lipid emulsion character of blood serum is transitory, appearing only when the blood is called upon to distribute fatty food materials. More fundamentally, human serum is an about 7.5 per cent protein solution. The protein is a mixture of albumins and globulins. The globulins precipitate when serum is half saturated with ammonium sulphate and the albumins when it is fully saturated. In normal cases the albumin-globulin ratio varies from 4 to 1.2.<sup>23</sup>

Simply mixing the proteins and the other major serum constituents in the proper proportions does not give serum, because numerous vitally important biological properties depend upon the presence of traces of other materials. The point to be brought out here is, that with regard to its properties which are negligibly influenced by such traces of material, serum behaves just as would a synthetic solution of a mixture of two types of protein. Such properties are specific gravity,<sup>24</sup> viscosity,<sup>25</sup> refractivity,<sup>26</sup> and osmotic pressure.<sup>27</sup> The influence of protein on each of these is determined not only by the total amount of protein present, but also by the ratio of albumin to globulin, for the simple reason that the effect of 1 per cent of albumin is different from that of 1 per cent of globulin in each case.

Surface tension is an example of a property susceptible to the influence of the traces of material mentioned above. Thus in studying the

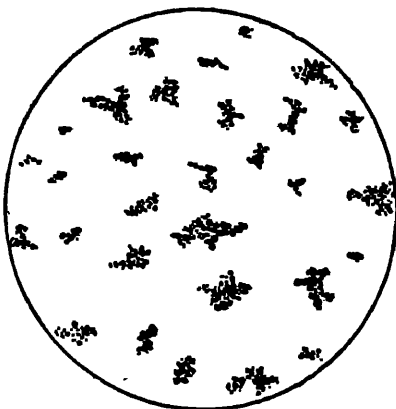


FIG. 10.

<sup>23</sup> Gram: *Am. J. Med. Sci.*, **168**, 511 (1924).

<sup>24</sup> Chick: *Biochem. J.*, **8**, 261 (1914); Chick and Lubrzynska: *Biochem. J.*, **8**, 59 (1914).

<sup>25</sup> Rohrer: *Deut. Arch. klin. Med.*, **121**, 221 (1916-17).

<sup>26</sup> Robertson: *J. Biol. Chem.*, **11**, 179 (1912).

<sup>27</sup> Govaerts: *Compt. rend. soc. biol.*, **93**, 441 (1925).

physico-chemical characteristics of immune sera Lecomte du Noüy<sup>28</sup> reports that there is no detectable difference in chemical composition as between normal and immune sera and that density, viscosity, refractive index, conductivity, etc., are unaltered. However, surface tension differences do appear and the undoubted biological differences between the two types of sera can be detected in certain cases by means of this property.

Human serum is not the most readily available material. A number of samples have been available to the writers in connection with routine examination of mental patients whose sera differ very little if at all from those in normal cases. The opportunity has been taken of compiling certain data in illustration of the behavior of human serum as an ordinary synthetic mixture of two types of proteins. This has involved the determination of relative viscosities using a 1-cc. Ostwald viscometer, specific gravities with a 1-cc. pycnometer, conductivities with a Christian-sen ionometer,<sup>29</sup> and protein contents from total nitrogen figures obtained by the Kjeldahl method. The viscosities and specific gravities were done at  $25 \pm .05^\circ$ , using a thermostat. It was shown experimentally that the pH differences involved were not sufficient to cause viscosity differences which were significant from the point of view of the demonstrations to be made.

Figure 11 shows the specific gravities plotted against the viscosities for about sixty sera. The specific gravity of blood serum depends upon the protein and crystalloidal contents. For a constant crystalloidal content we should expect a regular increase in specific gravity with increasing protein content in so far as variations in the albumin-globulin ratio do not interfere. It is known from the corresponding conductivity measurements that the salt variation was not sufficient to cause an appreciable variation in the distribution of the points, and further that high blood sugar and urea may be ruled out because none of the patients from whom these sera were obtained were suffering from diseases which bring these about. The crystalloidal contents can therefore be considered constant so far as this demonstration is concerned. The viscosity depends almost wholly upon the protein content. As opposed to the specific gravity, the viscosity of a protein solution ordinarily increases more rapidly than regularly with the protein content, resulting in the familiar curve convex to the protein-content axis when protein contents are plotted against viscosities.<sup>30</sup> However, over a small range of protein contents such as that in normal sera this relationship should closely approximate a straight line.

<sup>28</sup> Alexander's "Colloid Chemistry," 2, 775 (1928).

<sup>29</sup> Gram and Cullen: *J. Biol. Chem.*, 57, 477 (1923).

<sup>30</sup> Chick and Lubrzenska: *Biochem. J.*, 8, 59 (1914).

It follows that when plotting viscosities against specific gravities one should get pretty good straight lines except in so far as variation in the albumin-globulin ratios may modify the situation. Since the variations shown in Fig. 11 may readily be explained on this basis, the general result is quite in accord with the demonstration which is being made. With the possible exception of half a dozen points they may be explained on the basis of the normal variation of the albumin-globulin ratio.

The question of the slope of the line in Fig. 11 is rather interesting. If both specific gravity and viscosity varied regularly with the protein content, the continuation of this straight line should include the point of zero protein content, that is, approximately the point for the specific gravity and viscosity of Ringer's solution. However, the best straight line which could be drawn through the points to also include the point for Ringer's solution is shown by the dotted line in Fig. 11. The

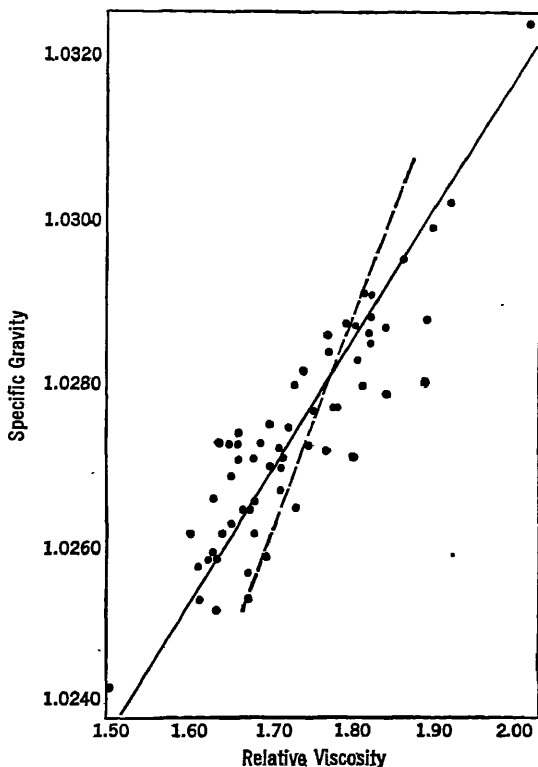


FIG. 11.

answer presumably rests in the fact of the regular increase in specific gravity with protein content as compared with the more rapid increase of viscosity.

The simplest way to test this hypothesis was to make various dilutions of sera with Ringer's solution and to measure the viscosity and specific gravity for each dilution, and then to plot them against dilution. This is in effect plotting them against protein content, since the crystalloidal content is kept approximately constant by using Ringer's solution as the diluent. The results are shown in Fig. 12. Each curve is drawn

through points from three experiments in which sera of closely the same protein content were used. The curvature of the viscosity curve is ample to account for the difference in slope between the line drawn through the

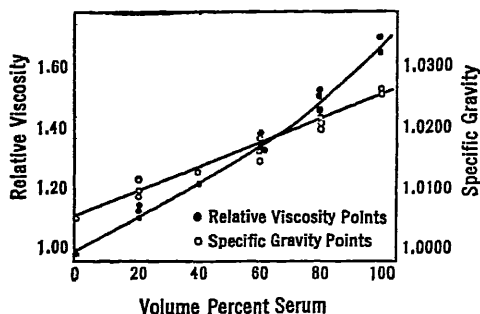


FIG. 12.

points in Fig. 11 and the dotted line which passes through the point of zero protein content. Figure 12 also brings out very nicely the difference in type between the specific gravity and viscosity curves.

The next step was to actually determine the protein contents of a series of sera and to plot them

against the corresponding specific gravities and viscosities. Choosing sera with points close to the straight line in Fig. 11, in order to have as closely as possible the same albumin-globulin ratios, a straight line should be obtained in the case of specific gravity and an approximate straight line in the case of viscosity. This prediction is verified very nicely as shown in Fig. 13.

The general conclusion is that with regard to specific gravity, viscosity, and protein-content relationships, human blood serum behaves as a simple synthetic solution of a mixture of two types of proteins. It is apparent that knowing the value for any one of the three gives a good idea of the values of the other two in any normal case.

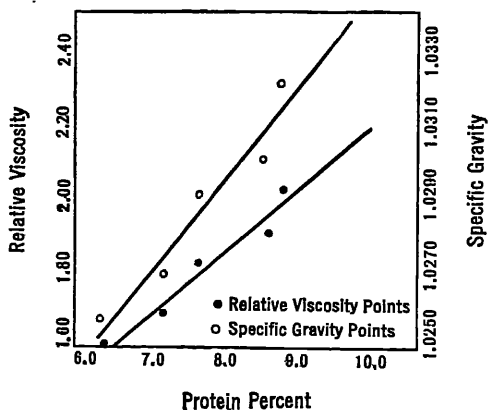


FIG. 13.

Getting back to the consideration of human serum in its dual aspect of lipid emulsion and protein solution, one would like to know the effect of the emulsion particles on the viscosities and specific gravities which have just been discussed. Actually these were measured on sera containing few chylomicrons, but the question is one of theoretical and practical interest.



A subject (one of us) had breakfast at seven-thirty and nothing more to eat until two o'clock that afternoon, when a blood specimen was taken. Four ounces of butter were then eaten with soda crackers and another blood specimen taken from one to two hours later. Under the dark-field microscope the serum from the first specimen looked like Fig. 14 and that from the second like Fig. 15. The increase in the number of chylomicrons is very marked. In spite of this, no significant change in the specific gravity would be expected on the basis of the possible change in fat content and the specific gravities of serum lipoids and whole serum. Einstein's law indicates that the increase in

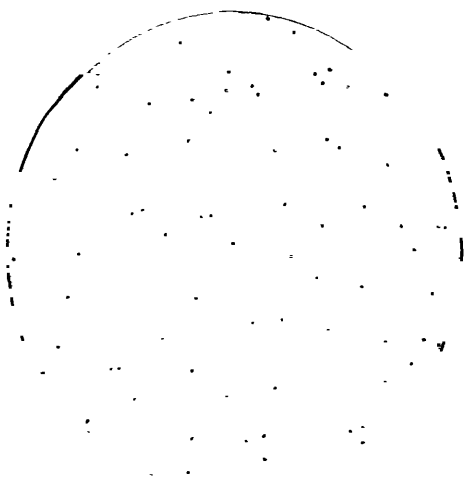


FIG. 14.

viscosity should be of the order of a few tenths of a per cent, well within the range of possible error due to pH difference.

Actually the specific gravities came out exactly the same, and the viscosities had increased by about one per cent, this amount being also in the range of possible error due to pH difference. Thus, in this case, a large increase in the number of chylomicrons caused no change in specific

FIG. 15.

gravity or viscosity detectable by the methods employed.

## SUMMARY

Human blood serum is not only a protein solution but, under ordinary conditions, also a lipid emulsion and hence of exceptional colloid interest from two points of view.

The determination of the relative number of lipid emulsion particles or chylomicrons is a rough measure of their relative contents of ether-extractable material. Evidence is presented which indicates the possibility of the use of the chylomicron count as an independent semi-quantitative method for determining free fat contents in normal sera.

The colloid chemistry of the chylomicrons has been a neglected field. Evidence is presented which affords strong indication that the chylomicron emulsion is stabilized by films of serum protein.

As a protein solution, human serum behaves as a synthetic solution of mixed albumins and globulins with regard to properties which are negligibly influenced by small amounts of materials of specific biological importance. Data are presented to illustrate this point for specific gravity, viscosity, and protein-content relationships.

In conclusion, an experiment is described which gives a preliminary bit of evidence as to the relative effects of the two types of colloid systems on certain physical properties of the whole serum.

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## THE LIESEGANG PHENOMENON IN GALL STONES

BY J. E. SWEET

THE study of magnified sections of many human gall stones reveals a structure such as that shown in Figs. 1, 2 and 3, concerning which there can be little doubt that we are looking upon an example of the phenomenon of rhythmic precipitation, commonly called the rings of Liesegang. The characteristics of the phenomenon are so evident in these more perfect gall stones that it is not necessary to discuss before a group of colloid chemists the old idea that these structures are the result of growth by the deposition of differently colored layers.

The concept is of evident importance to human pathology since the older idea assumed the building up of the structure around a nucleus with a radial arrangement of crystals. On the other hand, the recognition of these rings as beautiful examples in nature of rhythmic precipitation implies that the structure must have arisen as a mass composed of at least two substances, one of which, at least, must be in the colloid state, with a third substance capable of producing a chemical reaction with one of these substances, the resultant precipitate constituting the colored rings.

The facts seem to conform to the necessities of the hypothesis, in so far that two chemical substances are always present in the most common type of gall stones, the monatomic alcohol, cholesterol, which under certain circumstances can form a gel, and calcium, and in the surrounding bile is the characteristic coloring matter of the bile, bilirubin—or some of the products resulting from the oxidation of bilirubin—which is known to possess a strong affinity for calcium.

It seems probable that the gall stone forms as a mass of cholesterol and calcium in the colloid state, each, perhaps, mutually maintaining the other in this state. This plastic mass is moulded into form, which form is determined by the peculiar internal anatomy of the gall bladder, and sometimes, in addition, by the presence of previously formed stones, and then it becomes subject to the action of the bilirubin. The calcium precipitates as a calcium bilirubinate in rhythmic precipitation, forming rings of varied colors, and the consequence of this precipitation is the shifting of the cholesterol from the colloid to the crystalloid state. That the cholesterol passes into the crystalline state after the formation of the

rings is indicated by the fact that the crystal beams pass through the rings, as the crystals form from periphery to center.

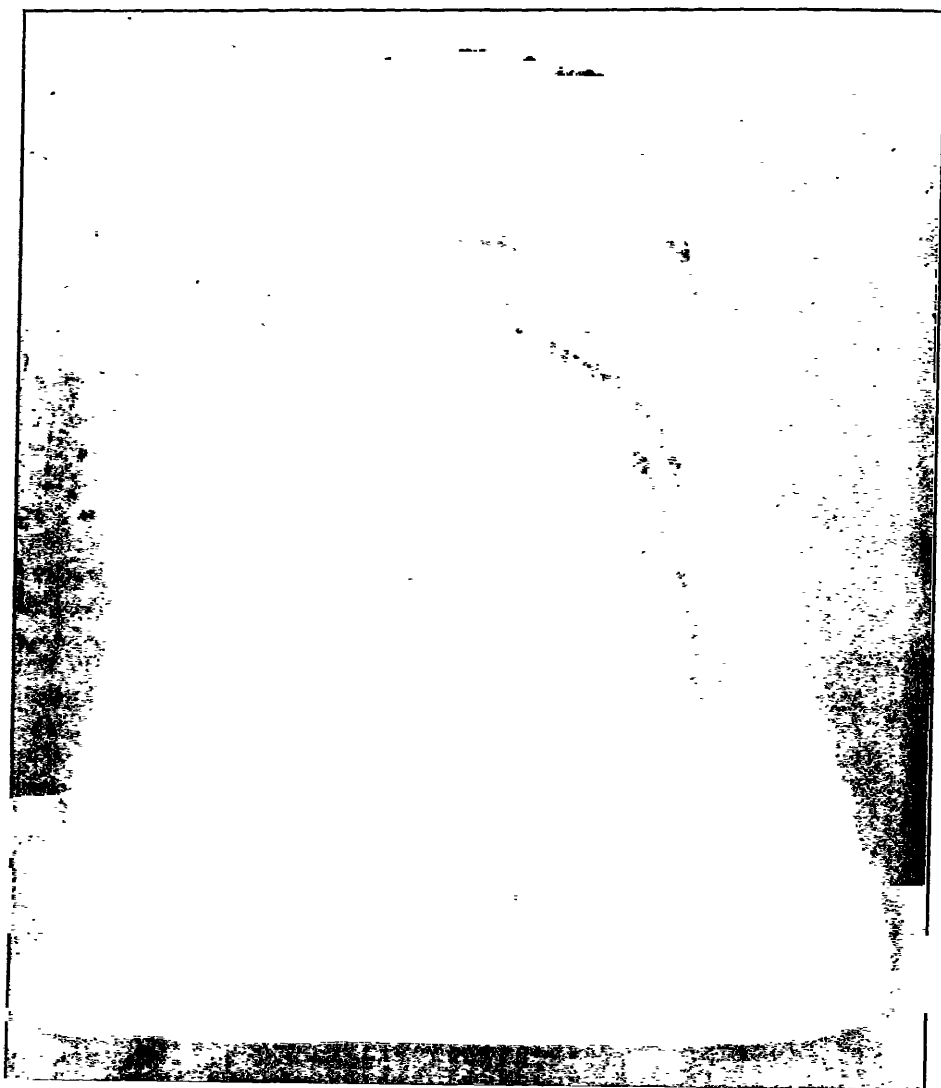


FIG. 1.—Cross-section of gall stone, polished, photographed under water. The rings of Liesegang as formed from the center outward.

The most common condition in the gall bladder seems to be that the bilirubin is on the outside of the colloidal mass, and the rings form from

the outside as in Figs. 2 and 3. More rarely, as seen in Fig. 1, it would seem that the colloidal mass must have surrounded and enclosed the



FIG. 2.—Cross-section of gall stone, with rings forming from the outside in.

bilirubin which then starts the formation of concentric rings from within outward.

When we come to study this reaction as occurring from the outside of the mass we find interesting results which seem to be determined by

the geometric form of the mass before us. I have not seen this particular point emphasized in the study of the phenomenon. Many of the round



FIG. 3.—Cross-section of gall stone, with rings forming from the outside.

or oval gall badder stones show a beautiful concentric-ring formation, Figs. 2 and 3, which can be duplicated in all details by the method I have used in obtaining these lantern slides. A thin sheet of dichromate

gelatin is poured upon a sheet of glass the size of the standard lantern slide. After the gelatin has set, various geometric forms are cut out and

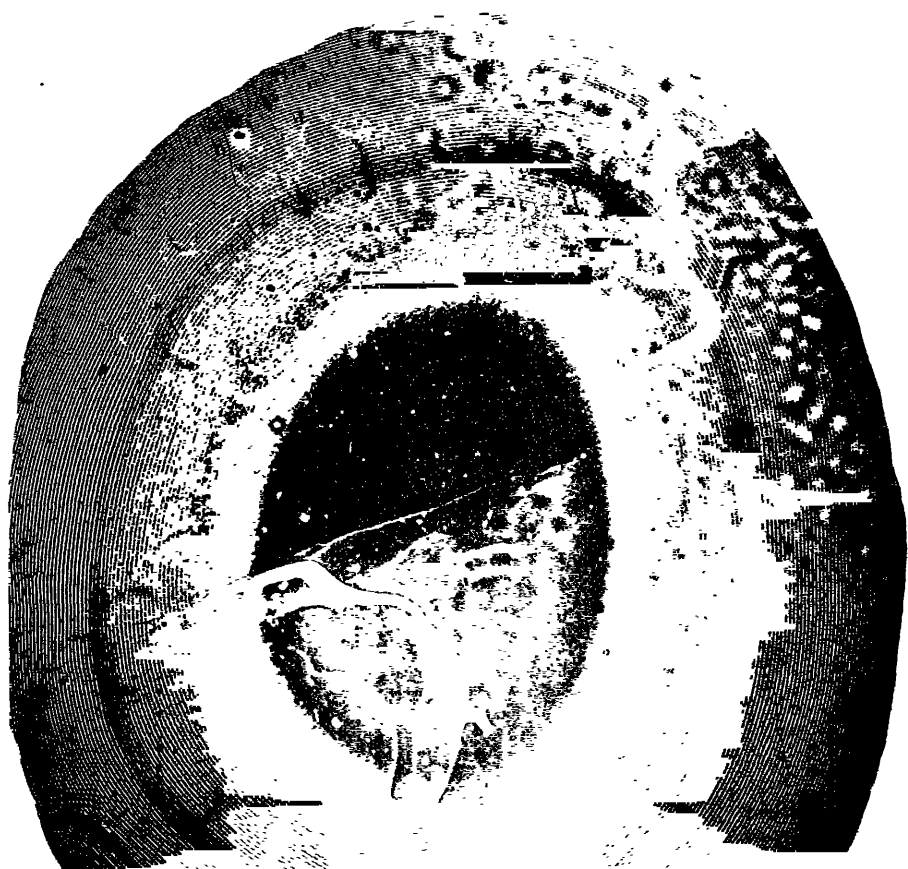


FIG. 4.—Concentric rings forming in a round mass of dichromate gelatin, the silver nitrate solution having been applied to the periphery.

silver nitrate solution is added either as a single drop in the center of these geometric forms, in order to obtain the effects seen in Fig. 1, or

else the solution is applied to the periphery of the gelatin, which produces peculiar results, dependent upon the geometric form. After the process has reached any desired stage, the silver nitrate can be washed off, and the sheet of gelatin allowed to dry. The preparation can then be

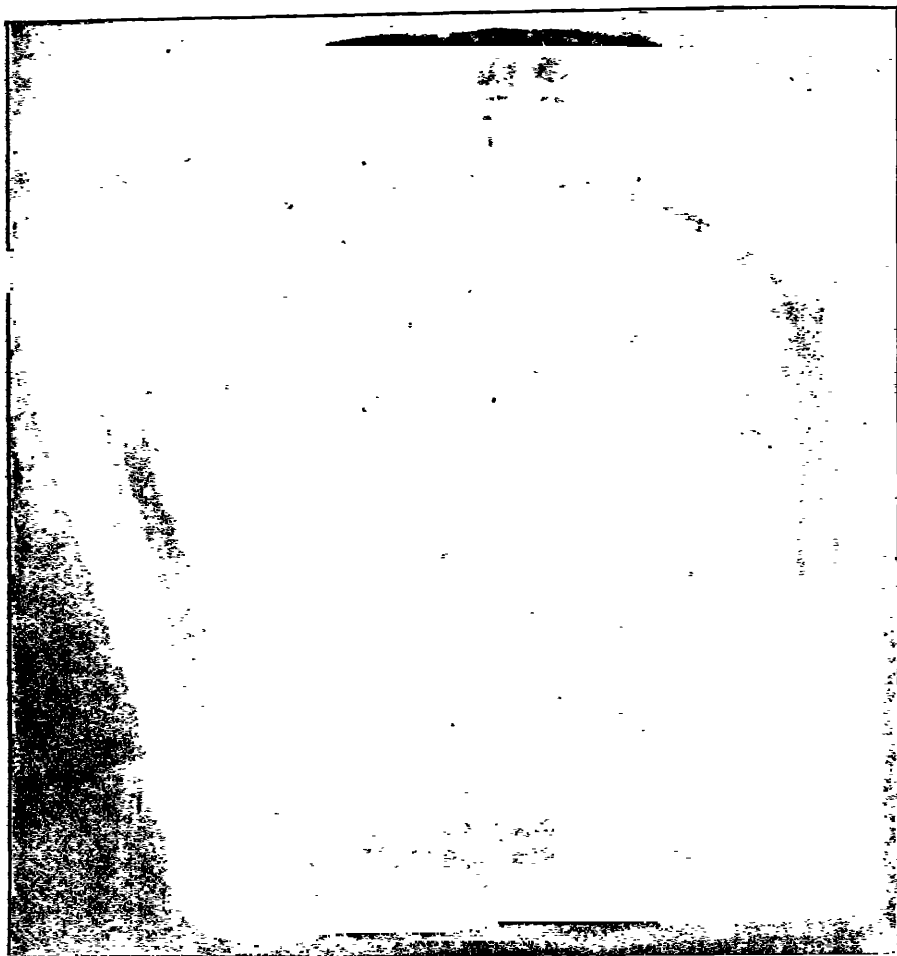


FIG. 5.—Cross-section of gall stone showing the disturbance of the ring formation at the angles.

mounted as a lantern slide, a method which permits the ready preparation of specimens for demonstration. The gelatin sheet must be kept in a moist chamber while the rings are forming to avoid too rapid drying out. It may be found useful to bring the silver nitrate solution to the edge of the gelatin by means of a camel's hair brush.



Such a procedure, when the silver nitrate is added to the periphery of a round or oval mass, results in the formation of perfect concentric

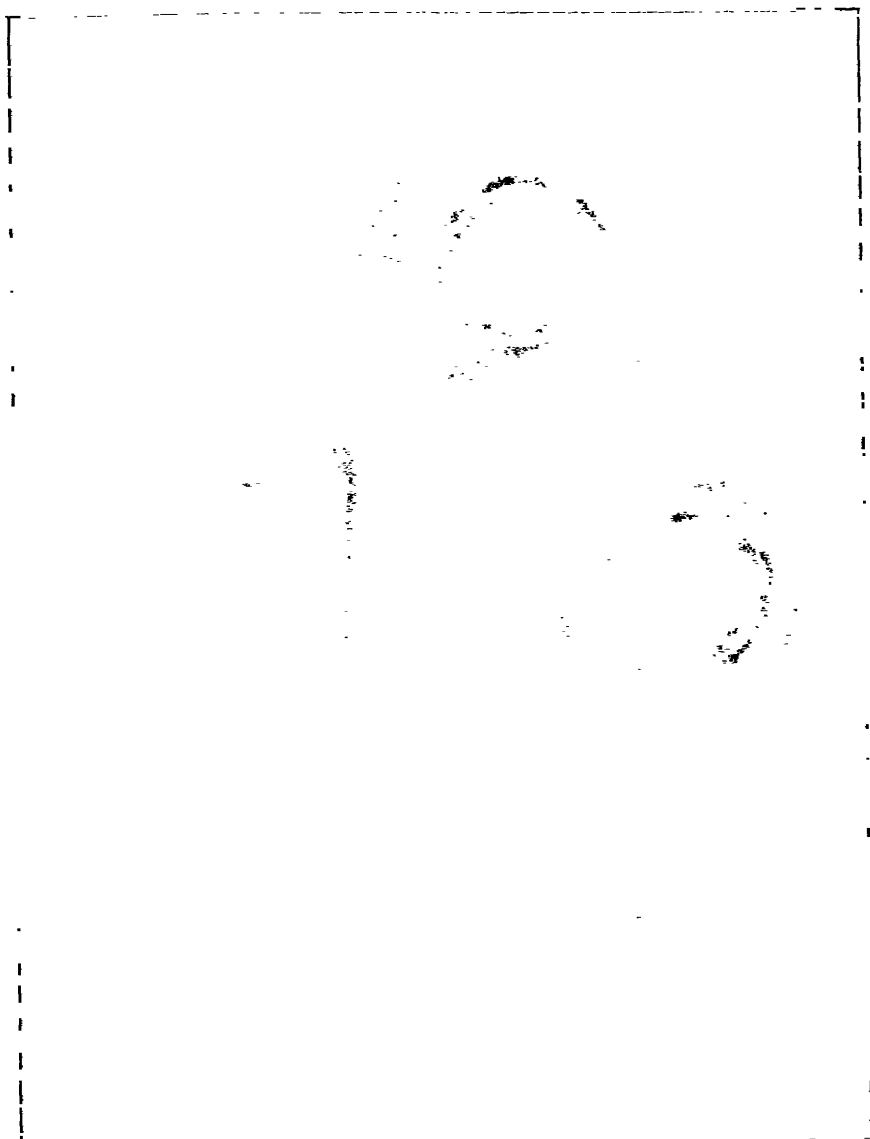


FIG. 6.—Cross-sections of gall stones, showing the relation of geometric form to ring formation.

rings as seen in Fig. 4. At times wider rings occur, at times a concentration of material in the exact center appears, forming an apparent nucleus.

It should be noted that we are dealing with the principles of plane geometry, whereas, in the actual gall stone we are dealing with forms of

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FIG. 7.—A square of dichromate gelatin showing the disturbance of ring formation at the angles. In the lower right-hand corner a tiny drop of silver nitrate solution causes a marked disturbance of the process.

three dimensions. If the dichromate gelatin be moulded in shapes comparable to actual gall stones and these masses are dropped into a solution

of silver nitrate, even more accurate duplications of the actual gall stones can be formed; but it is then difficult to obtain satisfactory cross-



FIG. 8.—A triangle of dichromate gelatin showing the effect of a more acute angle.

sections of these masses, and I have therefore found that the method first described is more satisfactory for the preparation of demonstration material.

Cross-sections of stones of various geometric form, as shown in Figs. 5 and 6, often show in the angles a condition which looks as though a different material were here being deposited. This point has been a stumbling block in the theory of the building up of gall stones by successive deposits. Let us apply our method of study to geometric forms of gelatin as in Fig. 7, and we find at the angles a condition entirely comparable to the findings at the angles of the actual gall stones. I would not presume, before this body, to enter into a discussion of the principles underlying the phenomenon of rhythmic precipitation. Diffusion is certainly essential to the process, and since diffusion must take place in a direction perpendicular to the surface, it is evident that a conflict of forces will occur at the angles. In the lower right-hand corner of Fig. 7 there is seen the interesting effect produced by the conflict of two forces—the one starting from the outside, and the other emanating from a tiny drop of silver nitrate, which accidentally fell upon the gelatin sheet. As the angle becomes more acute the disturbance becomes more marked as seen in Fig. 8.

So far as I am aware, attention has not been called heretofore to this relationship between the phenomenon of rhythmic precipitation, and the geometric form of the mass in which the process is taking place. It seems to me to demonstrate that the precipitates of coloring matter in human gall stones, not only in the rarely perfect examples, such as seen in Figs. 1, 2, and 3, but in the less apparent conditions as seen in Figs. 4, 5, and 6, are all but modifications of the same process, a process subject to infinite variation of shape and size of the mass in which the process is taking place, to infinite variation due to different concentrations of the reacting substances, to the presence of impurities, variations of surface tension, etc. It is possible that the same principle will be found to apply to many other instances of this interesting phenomenon of rhythmic reaction.

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# STUDIES ON THE POROUS DISC METHOD OF MEASURING OSMOTIC PRESSURE

BY J. C. W. FRAZER

## I. INTRODUCTION

THIS problem was undertaken with the object of obtaining accurate direct measurements of osmotic pressure of electrolytes in dilute aqueous solutions. Compared with other colligative properties of solutions, osmotic pressure offers a means of obtaining an accuracy difficult of attainment by other methods such as freezing point lowering, etc.

The porous disc method for measuring osmotic pressure developed by Frazer and Patrick<sup>1</sup> of this laboratory and used by Townend<sup>2</sup> overcomes many of the difficulties encountered in using membranes of the usual type. While it seems that the porous disc method is difficult to manipulate, it is hoped that sufficient information regarding the proper conditions necessary will be obtained to simplify its use.

The method here described makes use of an earlier observation by Askenasy,<sup>3</sup> in which plant physiologists have taken much interest. He found that water in contact with a porous disc could, on evaporating through the disc, produce tensions greater than atmospheric.

We may define osmotic pressure as the pressure difference necessary to put the solution and solvent in equilibrium. The mechanism by which this is accomplished in the usual osmotic pressure experiments is to separate solution and solvent by a semipermeable membrane. It is then possible to bring pressure on the solution until equilibrium is established. On the other hand, it is possible to produce equilibrium between the solution and solvent by subjecting the solvent to a tension. The mechanism by which we are attempting to bring this about is the utilization of the experiment of Askenasy.

<sup>1</sup> Frazer and Patrick: *Z. physik. Chem.*, **130**, 691 (1927).

<sup>2</sup> Dissertation, Johns Hopkins University (1927); *J. Am. Chem. Soc.*, **50**, 2958 (1928).

<sup>3</sup> "Beiträge zur Erklärung des Saftsteingens," *Verhandl. des naturh. med. Vereins zu Heidelberg*, **5** (1896).

## II. DESCRIPTION OF THE APPARATUS

The apparatus which was used in this work is shown in Plate I. The entire apparatus was constructed of pyrex glass.

*A* leads to the vacuum pumps, *B* is a trap which in use was surrounded by a thermos flask containing solid carbon dioxide in gasoline. This trap served to remove water vapor for the protection of the vacuum pumps and could be drained by breaking the tip at the bottom. Trap I serves to isolate the entire system from the outside. *B'* is a tube for condensing water vapor when desired by simply bringing up a beaker of

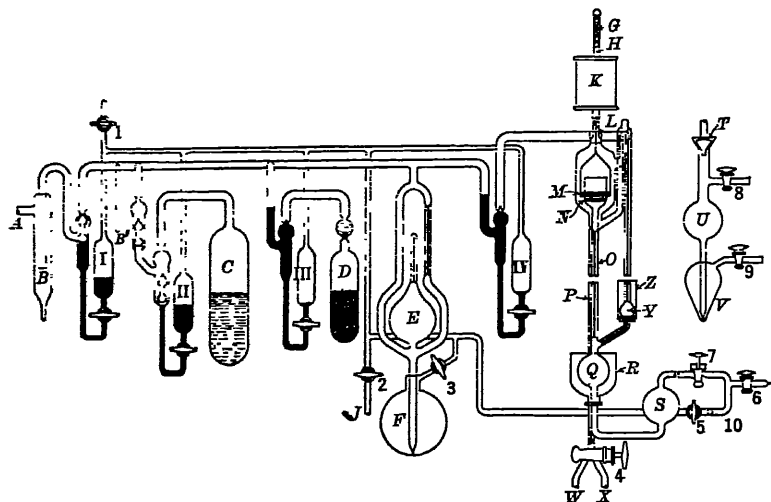


PLATE I.

ice and water around it. Bulb *C* is a water deaeration bulb. The trap II was made double so that the water could be heated without forcing vapors through the mercury of the trap. The upper trap was never completely closed, in order that a cushion would be present to take care of expansion of mercury if it became hot. A side tube at the top of *C* surrounded by a water jacket to condense and reflux water is not shown in the diagram. Another water deaeration bulb similar to *C* and not shown in the diagram was also used. In its construction the water jacket was made to surround the vertical outlet tube of the bulb. The bulb *D* contains cocoanut charcoal. *E* is the McLeod gage.

Beyond trap IV is the apparatus called the osmometer. The large bulb not designated on the diagram will be referred to as the cell. *N* is the porous disc sealed into a cup open at the top and sealed to capillary *O* at the bottom. *M* is a platinum gauze ring for stirring the solution,

it being pulled up and down by spring *G* and solenoid *K* acting on *H* which is a sealed glass tube containing a soft iron core. The tube containing *G* and *H* is joined to the cell by an ungreased ground glass joint, *L*, sealed with mercury. Capillary tube *P* connects the cell to stopcock 4 through which solution may be forced in or removed. Capillary *O* is a uniform capillary communicating between mercury reservoir *Q* and the under side of the disc; *Y* and *Z*, a condenser for the water to be used under the disc were moved to a position at the top of the outer capillary to avoid the difficulties encountered in handling the water. Reservoir *S* was changed to a position with respect to *Q* identical with the arrangement of *V* and *U* in the separate diagram to the right. *S* served as a mercury reservoir over which the pressure of air could be regulated by manipulation of stopcocks 5, 6, and 7 to raise or lower the mercury in the capillary tubes above reservoir *Q*.

A secondary system connected to a mechanical vacuum pump at *J* served to operate the various traps and reservoirs by evacuation through *J* or entry of air through stopcock 1 later placed just above stopcock 2.

The separate diagram shown at the right is the "solution introducer." This could be brought up to the open ground glass stopper *T* which was attached to *W*. Stopcock 8 was later placed above *T* and sealed directly to the secondary system. Stopcock 9 was also removed and the tube from *V* connected to the secondary system by a rubber tube and a three-way stopcock with one limb open to the air, thus facilitating the regulation of air pressure over the mercury in reservoir *V*.

### III. EXPERIMENTAL PROCESSES<sup>4</sup>

*Requirements of the Method.*—Several conditions must be met in order successfully to use this method for determining osmotic pressure of dilute aqueous solutions. The temperature must be kept constant. The porous disc must necessarily be thoroughly clean and thoroughly air-free. A disc with soluble matter in it would cause contamination of the pure water and thus give results which would be too low, and the presence of air, even in the most minute amounts if trapped in porous pockets on the under side of the disc would cause the water to fall away from the disc when tension is applied. Air-free water is necessary, especially that which is to be used under the disc, as the presence of air would increase the likelihood of the water forming a vapor bubble and thus falling away from the disc when tension is applied. The solution when made must be rendered as air-free as practicable and introduced into the apparatus without admixture with air. An analytical method must be devised by which small volumes of very dilute solutions may be

<sup>4</sup> The experimental work was done by F. T. Martin and L. H. Schultz.

analyzed with considerable accuracy. A satisfactory instrument for accurate observation must be used.

*Temperature Control.*—During a determination uniform temperature control was essential, especially as the solution being in the outer part of the cell would receive the effects of temperature variation from the outside before the pure water under the disc.

The thermostat was a well-insulated cylindrical copper tank of one meter height and diameter. The regulator consisted of a large helix of copper tubing filled with carefully purified toluene and sealed to a glass mercury bulb in which the electrical contact was made in a capillary. It was heated intermittently electrically and cooled continuously by water of constant temperature and flowing at constant rate. Variations of a few ten-thousandths of a degree were observed during determinations.

*The Cleansing and Deaerating of the Disc.*—The porous disc was prepared from a mixture of equal parts of finely ground pyrex glass and clay. This mixture was molded into the desired shape while wet and subsequently burned at about 900° C. It was found that such discs could be sealed readily into the pyrex glass funnel. The disc was then subjected to careful treatment to remove all grease and water-soluble material. Before use it was shown that water of low conductance after passing very slowly through the disc did not increase in conductance.

Complete deaeration of the disc and water in *C* was a task of several weeks. When in air-free condition there was no tendency shown by the water beneath the disc to pull away at any of the tensions used.

The progress of deaeration of the water in *C* is best shown in the following table, which gives in the first column the time elapsed after sealing the bulb, in the second the air pressure indicated when tested, and in the third the time elapsed between the last previous removal of vapor and the test, that would be the time during which the air accumulated in the vapor space:

Time after Sealing Bulb	Pressure in Millimeters Mercury	Time of Accumulation
4 hours	$2.5 \times 10^{-4}$	4 hours
8 days	$5 \times 10^{-5}$	2 days
12 days	$2 \times 10^{-4}$	overnight
24 days	$3 \times 10^{-5}$	overnight
36 days	$5 \times 10^{-5}$	2 days
78 days	$1 \times 10^{-3}$	42 days
86 days	$2 \times 10^{-5}$	5 days
95 days	$2 \times 10^{-5}$	5 days
105 days	$2 \times 10^{-5}$	5 days



The thoroughly air-free water showed no tendency to boil or become agitated even when opened directly to the high vacuum pumping system. With more diligent pursuit of the heating than was used, the time required to obtain the above results might doubtless be shortened.

*Sticking the Water to the Disc.*—Air-free water from *C* was distilled into the reservoir *Q* and was then forced up beneath the disc by means of mercury. Any excess could be easily evaporated and the level of the mercury meniscus in *O* adjusted to the desired position.

The water used in the apparatus had a conductivity of 0.7 to  $1.2 \times 10^{-6}$ .

*Preparation and Introduction of the Solution.*—The solution almost air-free was introduced into the osmometer by means of the apparatus mentioned above. This was connected to *X* by a ground and mercury sealed joint and when desired the solution was forced through stopcock 4 which was left mercury sealed. Complete removal of air was accomplished in the osmometer.

*Procedure in Making Measurements.*—The necessary data for the determinations consisted of measurements of temperature, the position of the surface of the solution, the position of mercury meniscus beneath the disc in capillary tube *O* called the upper meniscus, the time at which position of upper meniscus was determined, the position of the mercury meniscus in the outer capillary tube of the osmometer called the lower meniscus, and the position of some point of reference on the apparatus as a whole.

The various positions enumerated were determined by means of a cathetometer provided with a micrometer which was graduated in hundredths of millimeters.

*Removal and Analysis of Solution.*—The analysis of small samples of very dilute solutions presented some difficulties. For this purpose the interferometer had been used in this laboratory with fair success. For electrolytes it was decided to try to use conductance for determining concentrations, first setting up a curve from determinations of conductance on solutions of known concentrations and locating for the solution to be analyzed, the point on the curve representing the concentration corresponding to its conductance. Under favorable conditions conductance should be determinable to 0.1 per cent until dilutions are reached at which local conditions, as the amount of carbon dioxide or other soluble gases in the air, would affect considerably the results.

The cell designed for the purpose had a capacity of 18 cc. Electrodes were firmly sealed in the cell and platinized. It was fitted with a ground-glass stopper similar to *T*, Plate I, and joining the osmometer under the stopcock 4 through limb *W*. Samples of solution to be

analyzed were dropped into the cell after the latter had been evacuated by the secondary system joined to *W* by a stopcock. The conductivity cell was mercury sealed at the ground joint. As all of the mercury could not be removed after use the inlet tube of the cell formed a *U* and entered at the bottom in order to catch any falling mercury when the cell was removed. Insufficient work was done on the use of conductivity under the conditions prevailing to make a guarantee of any definite maximum limit of error, though the error was probably not greater than about 1.5 per cent. The two series of measurements made were in as good agreement with each other as were the individual points in either series, so all of the points were plotted together in drawing the curve. For potassium chloride the curve is practically a straight line.<sup>5</sup>

The measurements were not made at the same temperature, so all have been calculated by application of a temperature correction to 26° C., using the formula

$$K_0 = K_t(1 + c(t_0 - t))^6$$

The value used for *C* was .0217. The conductances here given are not specific conductances, but the reciprocal resistances for the cell used. Concentrations are in terms of mols potassium chloride in 1000 gm. of water correcting to vacuum weight.

The results of conductance measurements on potassium chloride solutions are shown in Table 1 and Fig. 1.

TABLE 1—CONDUCTIVITY OF POTASSIUM CHLORIDE

Series I		Series II	
Concentration	Conductivity	Concentration	Conductivity
.01192	.01326	.00048	.00058
.00492	.00561	.00060	.00082
.00326	.00375	.00107	.00125
.00185	.00223	.00269	.00309
.000860	.00106	.00432	.00497
.000394	.00053	.00729	.00810

*Preparation of a New Dilution.*—A series of measurements on any one solution was made by using first the most concentrated solution

<sup>5</sup> Kohlrausch and Holborn: "Leitvermögen der Electrolyte," Leipzig, 110 (1898).

<sup>6</sup> Landolt and Börnstein: "Tabellen," 5th Ed., 1092.

which the apparatus would serve as limited by the length of the dry tube under the disc and the length of the window of the postat. Thus the limit in these experiments was to solutions under normal for a highly dissociated uni-univalent salt as potassium chloride. A desirable position for the surface of the solution was such that the stirrer in its highest position was still partially immersed. The

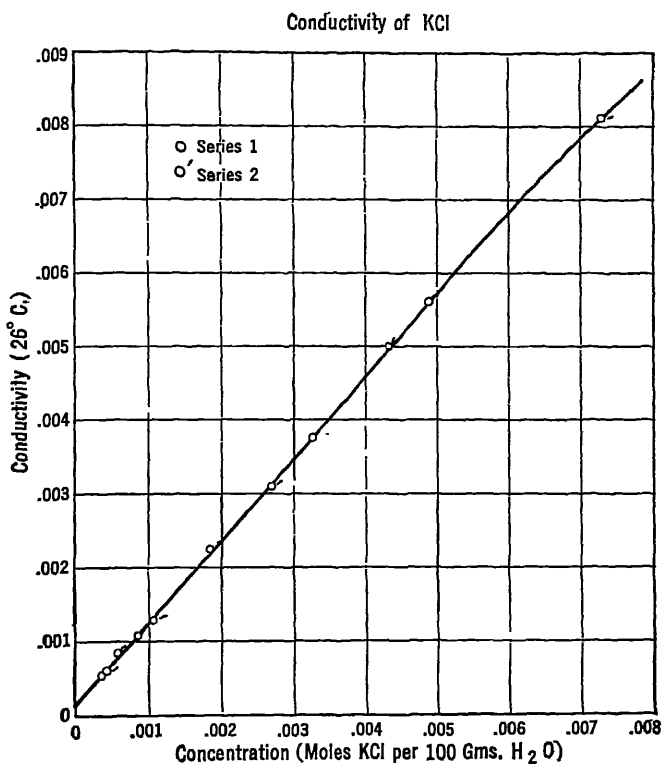


FIG. 1.

then contained from 60 cc. to 70 cc. of solution. A sample was then added to the conductance cell for analysis and as the conductance required about 18 cc. about 40 cc. of original solution remained.

To prepare a new dilution traps II and IV were opened to the bulb containing air-free water and the required amount of air-free water added into the solution.

## EXPERIMENTAL RESULTS

Of the eleven series run, six will be tabulated and represented by graphs in this paper. The preliminary series not shown here revealed a very great source of error in the arrangement of the apparatus. The results in these cases indicated osmotic pressures far above those which could reasonably be expected from solutions of the concentration known to be present. This suggested that distillation was taking place to some other part of the system than the solution.

The reason for the extremely high results mentioned was found to be the cooling effect of evaporation from the surface of the water in the thermostat. Certain parts of the osmometer extended above this surface, and although the whole was covered and the room temperature was kept always higher than that of the thermostat a deposit of tiny droplets of moisture was noted on the inside of the glass tubes at the points where they passed through the surface of the water in the tank. This cooling was eliminated by pouring light paraffin oil over the surface of the water, thus preventing evaporation.

The results of later series are given in tables and graphs below. The method of calculating some of these items has already been explained. The total average tension, given in terms of millimeters of mercury at  $0^{\circ}\text{C.}$ , was calculated by considering the tension from the lower mercury meniscus to the surface of the solution as consisting of three parts, namely, mercury height, height of water from upper mercury meniscus to disc, and height of vapor from disc to surface of solution. The last two of these can be expressed together in terms of water, as at equilibrium conditions the pure water would be in equilibrium with its vapor at all heights. As the lower meniscus moved slightly but not at constant rate, the average of its position was considered, while for the upper meniscus the mean position was taken for calculation of tension, the rate of change in this case being constant for any one tension. A slight addition for the difference in pressure on the lower mercury meniscus and the corresponding pressure if the tension were entirely due to a water column, in which case the lower meniscus would be much lower, was found on calculation to be entirely too small to demand consideration.

In series 1 a column of water rested on the lower mercury meniscus and its height was subtracted from that of the water column above the upper mercury meniscus. In all other series the lower meniscus was dry. Reference point to determine shifting in the apparatus was not used until series 5. The curves in Fig. 6 show points for both corrected and uncorrected positions to illustrate the value of such a point of reference.

The total average tension was calculated from the following simple expression used simply for convenience.

Tension in millimeters of mercury at 0° C.

$$= (U - L) \frac{D_i}{D_0} + (S - U) \frac{d_i}{D_0},$$

where  $L$  = position of lower mercury meniscus;

$U$  = position of upper mercury meniscus;

$S$  = position of surface of solution;

$D$  = density of mercury;

$d$  = density of water.

#### SERIES 1. KCl

Temperature (average).....	26.4555°
Conductivity of sample (ohms <sup>-1</sup> ).....	.005742
Concentration of solution (mols KCl/1000 g. H <sub>2</sub> O).....	.00504
Indicated osmotic pressure (millimeters mercury at 0° C.).	187

#### Series 1 KCl

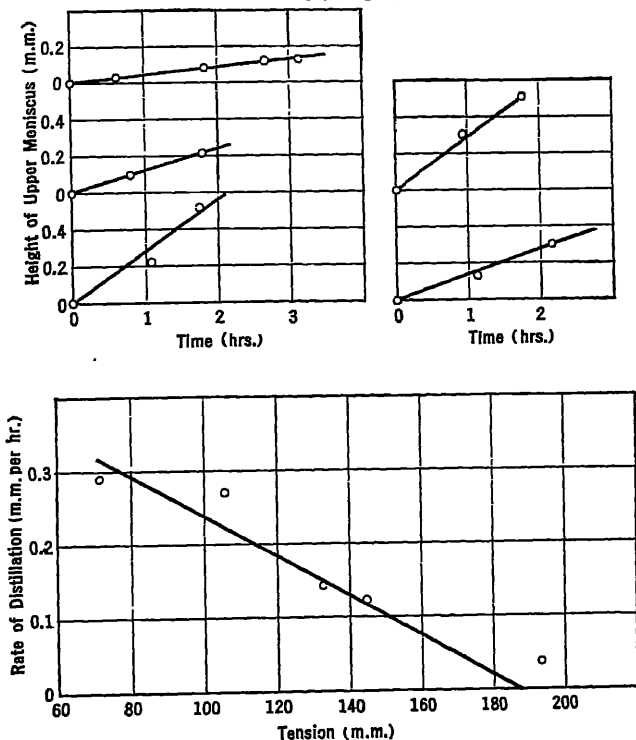


FIG. 2.

POROUS DISC METHOD OF MEASURING OSMOTIC PRESSURE

The graphical representations are in two parts. The curves on the upper halves of the sheets show for each tension used the positions of the upper meniscus referred to its initial position plotted against time in hours. The slopes determined from the above were taken to represent

SERIES 2. KCl

Temperature (average).....	26.4542°
Conductivity of sample (ohm <sup>-1</sup> ).....	.00344
Concentration of solution (mols KCl/1000 g. H <sub>2</sub> O).....	.00298
Indicated osmotic pressure (millimeters mercury at 0° C.).	112.4

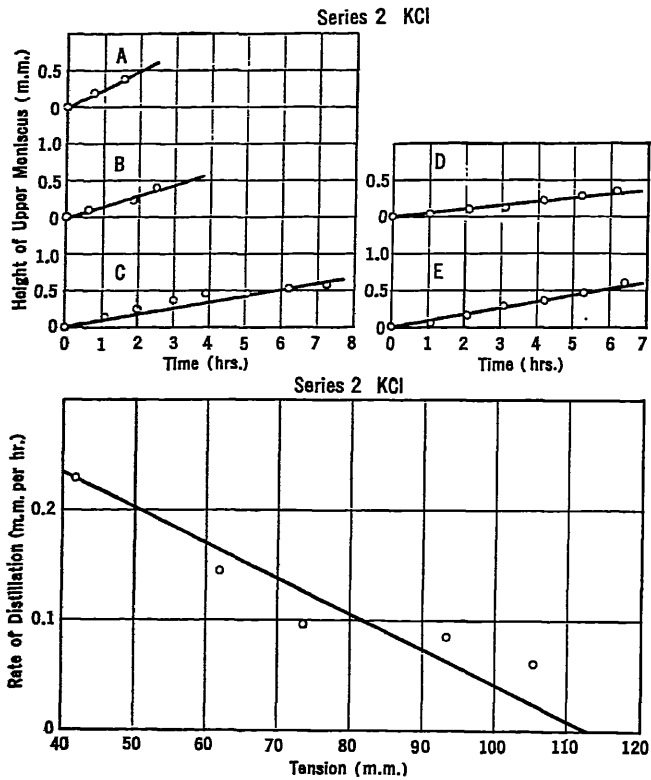


FIG. 3.

rates of distillation. On the lower halves of the sheets are shown the rates determined above plotted against the corresponding tensions. A straight line through these points is extended through the axis of zero rate to the tension corresponding to the point of intersection was taken as the osmotic pressure indicated by the experiment.

## DISCUSSION OF THE RESULTS

As will be readily seen by reference to the lower curves of Figs. 2, 4, 5, and 6, it is not possible to determine an accurate relation between rates and tensions from the results obtained. A straight line

## SERIES 3. KCl

Temperature (average).....	26.4555°
Conductivity of sample ( $\text{ohm}^{-1}$ ).....	.00344
Concentration of sample (mols KCl/1000 g. $\text{H}_2\text{O}$ ).....	.00298
Indicated osmotic pressure (millimeters mercury at 0° C.).	111.5

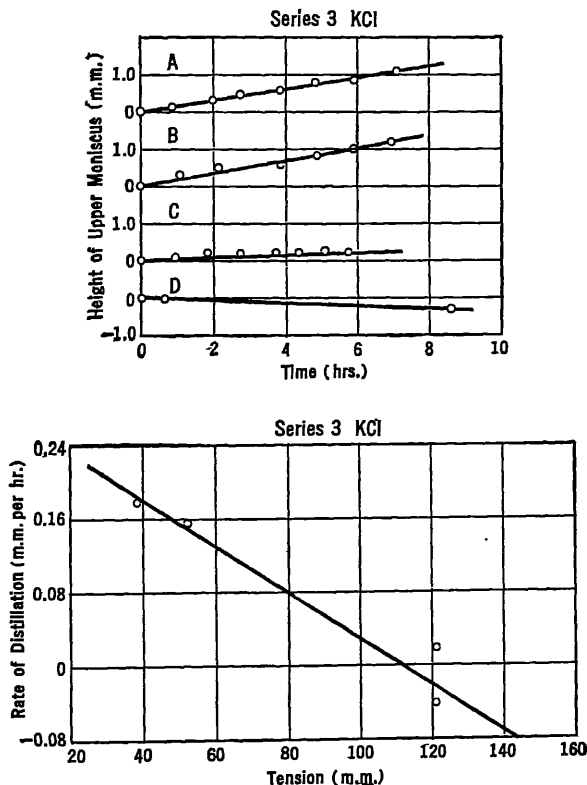


FIG. 4.

as in each case been drawn which gives approximately equal weight points on either side. The points of intersection of these lines with the axis of zero rate would indicate the osmotic pressure of the solution if the points were sufficiently consistent to determine the slope of the line accurately. Fig. 2 for results on a 0.00504 molal solution indicates

an osmotic pressure of 187 mm. for which the value of the van't Hoff factor  $i$  is 1.986. However, as is quite apparent, it would have been an easy matter to make the line intersect at points over a considerable range. Figs. 3, 4, and 5 are all for the same solution which was .00298 molal. The points of intersection of rate-tension curves with axis of zero rate of distillation for the lines drawn indicate osmotic pressures 112.2 mm., 111.5 mm., and 136.5 mm., respectively. The corresponding values for the factor  $i$  are 2.015, 2.005, and 2.45, respectively. Series 5, shown in Fig. 6 for a solution .0020 molal, indicates an osmotic pressure 95 mm. which yields on calculation a value for  $i$  of 2.54. No attempt will be made to interpret the results as they are not consistent among themselves. The error must be in the conduct of the experiment.

An examination of the data showed no apparent relation between the temperature changes observed and abnormal results. For large changes in temperature the effects on the results were very apparent, but for variations even of a few thousandths of a degree it was difficult to find any effect on the results. Perhaps after elimination of other sources of error the effects of temperature changes will become more apparent. It is felt that where slight fluctuations in temperature occur at close intervals there is compensation, as the effect of a slight increase in temperature would be counterbalanced by the effect of a correspondingly great decrease.

In Fig. 6 are shown the results of the first series in which a point of reference to determine shifts in the apparatus as a whole was used. The value of choosing such a point of reference is immediately apparent when one considers the case of the last value given for tension  $A$ . On the curves in the upper half of Fig. 6 are plotted both the positions read and the positions applying correction for shift in reference point.

The four preliminary series not recorded in this paper yielded results which were nearly 100 per cent too high. As the great source of error was found to be distillation to other parts of the system than the solution it is considered probable that the same may still be the case to a much lesser extent. It is proposed to test this possibility by putting pure water in place of the solution to see if there will still be distillation from the disc. The ground glass stopper of trap IV is known to be moist, which may be the cause of the trouble. A plain Y mercury trap will be placed between it and the osmometer, thus avoiding possible distillation to the trap.

One fact which was of considerable interest and considered of value in developing the use of the porous disc method was that distillation backward through the disc could be made to proceed as smoothly and

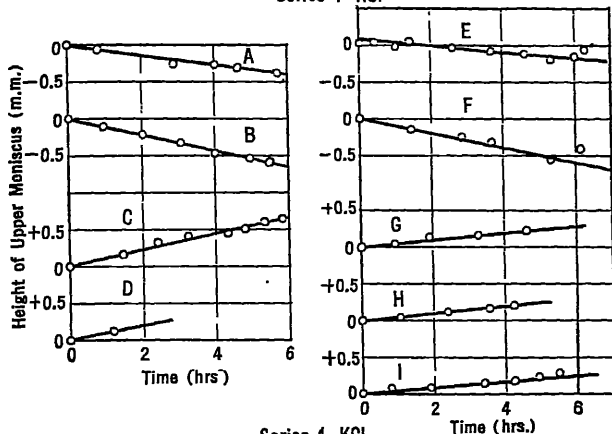


consistently as the forward distillations. This was first accomplished in series 3 and subsequently there was no difficulty in causing distillations back through the disc. In Fig. 4, *C* and *D* are for the

#### SERIES 4. KCl

Temperature (average).....	26.428°
Conductivity of sample (ohm <sup>-1</sup> ).....	.00344
Concentration of solution (mols KCl/1000 g. H <sub>2</sub> O).....	.00298
Indicated osmotic pressure (millimeters mercury at 0° C.).	136.5

#### Series 4 KCl



#### Series 4 KCl

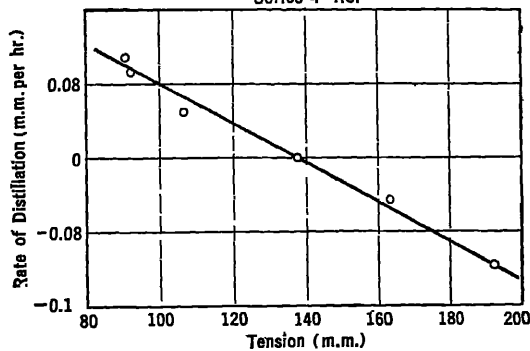


FIG. 5.

me tension, and it will be noted that the last reading of *C* showed a backward movement of the upper meniscus. This was allowed to continue and the results under the heading *D* were obtained. Previously it had been suggested that distillation backward was possibly prevented by the slow dissipation of the heat of condensation. This appears not

be the case and it is suggested that air in the pores of the disc prevented it, and that when through long use in forward distillations the disc was sufficiently swept clear of air the water molecules had greater freedom in entering the pores of the disc.

### SERIES 5. KCl

Temperature (average).....	26.429°
Conductivity of sample.....	.002343
Concentration of solution (mols KCl/1000 g. H <sub>2</sub> O).....	.0020
Indicated osmotic pressure (millimeters mercury at 0° C.).....	95.

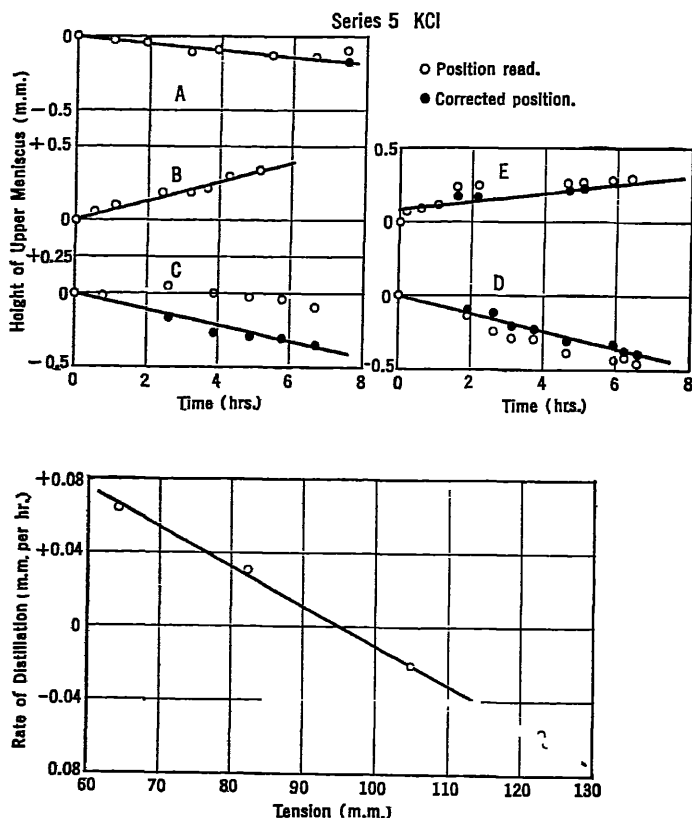


FIG. 6.

The effects of stirring were also observed in the course of the experiment to see if any effect other than rate of distillation could be observed. Trial without any stirring simply slowed down both the forward and backward distillation without changing appreciably the point of inter-

section of the rate-tension curve and the axis of zero rate. This matter should be given more study after other conditions have been improved.

### CONCLUSION

The results which are given above are not to be taken as correct measurements for the osmotic pressure of the solutions mentioned. Two difficulties have stood in the way of obtaining exact data. One of these was the removal of permanent gases, the other the control of temperature. The first of these difficulties has been overcome. This is not true of the second difficulty. We are quite sure that we do not have the necessary uniformity of temperature in our apparatus and when permanent gases have been removed from the system we have found that a small distillation other than that between solution and solvent has taken place. In order to be sure that the results obtained represent true osmotic pressure it must be shown that solvent distillation takes place only between solution and solvent. The proof of this will be given when with pure solvent replacing the solution in the apparatus described above, the point of zero distillation will correspond to that of zero tension on the solvent beneath the disc.

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# ADSORPTION AND THE PERMEABILITY OF MEMBRANES

BY HARRY B. WEISER

## I. INTRODUCTION

A MEMBRANE is said to be semipermeable when it permits one constituent of a solution to pass through—usually water—and does not allow diffusion of the other constituents or one or more of the other constituents. The plasma membranes of cells are natural membranes of this kind. Traube<sup>1</sup> was the first to recognize a similar semipermeability in certain gelatinous precipitates, the so-called precipitation membranes of which copper ferrocyanide is the most familiar example.

To account for the action of semipermeable membranes, Traube conceived of them as atomic or molecular sieves through which progressively larger molecules diffused with increasing difficulty. Thus a copper ferrocyanide membrane was believed to contain pores large enough for the small molecules of water to get through but too small to allow the larger molecules of sugar to pass. This view was shown to be inadequate by the observations of Tammann,<sup>2</sup> Walden,<sup>3</sup> I. Traube,<sup>4</sup> Barlow,<sup>5</sup> and others<sup>6</sup> who made comparative tests on a number of semipermeable membranes with a number of diffusing substances. If the action is that of a sieve, it should be possible to arrange the membranes in a series in the order of their permeability. On the contrary, it was found that a membrane quite impermeable to most substances may be more permeable to some than is a membrane which, in general, possesses high permeability. Moreover, the slight permeability of a membrane such as rubber to water and its high permeability to the much larger molecules of benzene and pyridine cannot be accounted for on the sieve theory.

The solution theory of the action of the semipermeable membrane postulates that a membrane is permeable to such substances as dissolve in it and impermeable to those that do not. This view was anticipated

<sup>1</sup> Archiv. Anat. Physiol., **86**, (1867).

<sup>2</sup> Z. physik. Chem., **10**, 255 (1892).

<sup>3</sup> Z. physik. Chem., **10**, 699 (1892).

<sup>4</sup> Phil. Mag., (6) **8**, 704 (1904).

<sup>5</sup> Phil. Mag., (6) **10**, 1 (1905); Findlay and Short: J. Chem. Soc., **87**, 819 (1905).

<sup>6</sup> Kahlenberg: J. Phys. Chem., **10**, 169 (1906).

by Liebig<sup>7</sup> as early as 1848 when he said: "The volume changes of two miscible liquids which are separated from each other by a membrane depends upon the unequal wetting or attraction which the membrane exerts on the two liquids." The first experimental work with the object in view of testing this theory was carried out by L'hermite<sup>8</sup> in 1855. In a test tube he placed some water, above this a thin layer of castor oil, and above this a layer of alcohol. In the course of a few days the alcohol had passed through the castor oil to the water, leaving but two layers in the tube. Turpentine was substituted for the oil with the same results. Again, when a layer of chloroform was separated from a layer of ether by a layer of water, the ether passed through the water to the chloroform. As a result of similar observations on eight different combinations of this kind, L'hermite reached the conclusion that substances which pass through membranes first dissolve in them. This mechanism has been supported by the work of numerous investigators.<sup>9</sup> Thus Kahlenberg found that benzene, toluene, and pyridine, which are soluble in rubber, diffuse through rubber, whereas water which is insoluble in rubber does not pass through.<sup>10</sup> Moreover, trichloroacetic acid passes through a rubber membrane when dissolved in benzene but only very slowly when dissolved in water.

While solution in the membrane may be a necessary and sufficient criterion for semipermeability in certain cases, Bigelow<sup>11</sup> and Bartell<sup>12</sup> demonstrated conclusively that osmotic effects can be obtained with inert material where neither solution nor chemical reactions can take place. Thus porous cups served as semipermeable membranes when the pores were sufficiently fine or when they were clogged to a certain extent with such substances as barium sulfate, lead chromate, lead sulfate, etc. Moreover, finely divided material such as silica, carbon, metallic copper, silver, and gold acted as semipermeable membranes when compressed

<sup>7</sup> "Ursachen der Säftebewegung," Braunschweig (1848); Liebig's Ann., **121**, 78 (1862).

<sup>8</sup> Ann. chim. phys., (3) **43**, 420 (1855).

<sup>9</sup> Graham: Phil. Trans., **144**, 177 (1854); **151**, 183 (1861); Nernst: Z. physik. Chem., **6**, 37 (1897); Tammann: *Ibid.*, **10**, 255 (1892); Overton: *Ibid.*, **22**, 189 (1897); Barlow: Phil. Mag., (6) **10**, 1 (1905); Kahlenberg: J. Phys. Chem., **10**, 169 (1906).

<sup>10</sup> Actually rubber dissolves or adsorbs water slightly and a rubber membrane is slightly permeable to water. Andrews and Johnston: J. Am. Chem. Soc., **46**, 640 (1924); Lowry and Kohman: J. Phys. Chem., **31**, 23 (1927); Schumacher and Ferguson: Ind. Eng. Chem., **21**, 158 (1929).

<sup>11</sup> J. Am. Chem. Soc., **29**, 1576, 1675 (1907); **31**, 1194 (1909); Bigelow and Robinson: J. Phys. Chem., **22**, 99, 153 (1918).

<sup>12</sup> J. Phys. Chem., **15**, 659 (1911); **16**, 318 (1912); J. Am. Chem. Soc., **36**, 646 (1914); **38**, 1029, 1036 (1916).

into discs containing very fine pores. The limits of the pore diameters between which osmosis can take place are not definitely known but they undoubtedly vary from substance to substance. Bartell found the upper limit to be around 0.9 micron with unglazed porcelain clogged with various materials. This is, of course, much too large to represent the dimensions of molecular interstices which Traube believed to be essential for semipermeability in membranes.

The osmotic phenomena observed with a distinctly porous non-soluble membrane such as a clogged porous plate, is doubtless the result of what is termed negative adsorption. If a solid adsorbent takes up relatively more of a solvent than of the dissolved substance the phenomenon is known as negative adsorption and the solution becomes more concentrated. Mathieu<sup>13</sup> observed this phenomenon with a number of solutions using porous plates, parchment and animal membranes, and single capillaries. With normal solutions the concentration in certain capillary spaces was found to be as low as 0.1 normal. The difference in concentration increases with decreasing radius of the capillaries and Mathieu concludes that with sufficiently fine capillaries water alone would be taken up: "The result of the investigation—that diluted aqueous solutions are formed not only in membranes but in general in capillary spaces if they are immersed in salt solutions—leads to a consideration of the properties of semipermeable membranes. If the capillaries in a semipermeable wall are considered to be so fine that only weak solutions can exist in them, one has an explanation of the fact that these walls in extreme cases are permeable for the pure solvent only."

The importance of negative adsorption for the theory of semipermeable membranes was recognized also by Nathansohn,<sup>14</sup> Bancroft,<sup>15</sup> and Tinker.<sup>16</sup> Thus Bancroft says:

If this conclusion is true and general, it accounts for the results of Bigelow and of Bartell, who found that osmotic phenomena appeared in porous cups when the pores were sufficiently fine or were clogged sufficiently. It is clear that we can get osmotic phenomena in two distinct ways, depending on whether we have a continuous film or a porous one. In the case of a continuous film, it is essential that the solvent shall dissolve in the membrane and that the solute shall not. Since the permeability is not dependent on adsorption, there is no reason why there should be any fundamental differences between the adsorption of a solute which does pass through the membrane and of one which does not pass through.

<sup>13</sup> *Ann. Physik.*, (4) 9, 340 (1902).

<sup>14</sup> *Jahrb. wiss. Botanik.*, 40, 431 (1904).

<sup>15</sup> *J. Phys. Chem.*, 21, 441 (1917).

<sup>16</sup> *Proc. Roy. Soc. (London)*, 92 A, 357 (1916); 93 A, 266 (1917).

With a porous film we shall get osmotic phenomena only when the negative adsorption is so marked that the pore walls adsorb practically pure solvent and when the diameters of the pores are so small that the adsorbed film of pure solvent fills the pores full. There is, therefore, an important difference between a solute which does pass through a membrane having very fine pores and one which does not pass through, in that the first is adsorbed by the membrane and the second is not.

Since a gelatinous precipitate consists of myriads of particles enmeshed into a network which entrains liquid,<sup>17</sup> it is probable that copper ferrocyanide membranes are porous in the sense that a fine porous plate is porous and are semipermeable toward sugar solutions therefore, because of strong negative adsorption. Tinker examined these artificial membranes microscopically and arrived at the conclusion that they are granular in character<sup>18</sup> with particles having diameters between 100 and 1000  $\mu$ . It is probable that the primary particles are much smaller than this and that what he was measuring was the diameter of secondary particles from partial agglomeration. In any event, it is difficult to see how even an approximate estimate of particle size could be arrived at from his published photographs. The important thing is that apparently independent of Mathieu, Nathansohn, or Bancroft, he concluded that negative adsorption in such a porous system is the primary cause of semipermeability. In support of this view, he demonstrated that cane sugar which ordinarily does not diffuse through a copper ferrocyanide membrane is adsorbed negatively by the salt. Ten-gram samples of finely divided copper ferrocyanide were shaken with sugar solutions of various strengths and the change in concentration determined polarimetrically. From this, the amount of water adsorbed was calculated. The results with four samples dried in different ways and to different degrees are given in Table 1. Correction was made for any water present in the adsorbent before immersing in the solution. It will be seen that sample 3, which has been dried in air, adsorbs the most water and sample 1, which was completely dehydrated in a hot oven adsorbs the least water. Complete dehydration is evidently accompanied by partial coalescence with consequent decrease in specific surface.

While the impermeability of a ferrocyanide membrane to sugar is doubtless due to the observed negative adsorption, the case of the impermeability of a copper ferrocyanide membrane to ferrocyanide ion cannot be disposed of in this way. That the ion does not pass the membrane

<sup>17</sup> Cf. Weiser: "The Hydrous Oxides," 13 (1926).

<sup>18</sup> Cf., also, Gurchot: *J. Phys. Chem.*, **30**, 99 (1926).



was pointed out by Tammann<sup>19</sup> and Walden<sup>20</sup> and confirmed by Donnan,<sup>21</sup> who tested his theory of membrane equilibria by placing potassium or sodium chloride on one side of a copper ferrocyanide membrane and potassium or sodium ferrocyanide on the opposite side. A Donnan equilibrium was set up as a result of the failure of the ferrocyanide ion to diffuse through. If Bancroft<sup>22</sup> is right in his contention, and he doubtless is, that there is no such thing as a molecular sieve for substances in true solution, then the membrane cannot be functioning as a sieve which screens out the relatively large ferrocyanide. As we shall see, the membrane is permeable to much larger molecules than

TABLE 1—ADSORPTION OF WATER FROM SUGAR SOLUTIONS BY  $\text{Cu}_2\text{Fe}(\text{CN})_6$ 

Approximate Strength of Cane Sugar Solutions, Per Cent	Water Adsorbed by 100 Gm. of Dry $\text{Cu}_2\text{Fe}(\text{CN})_6$			
	1 Dried Completely in Steam Oven	2 Dried over $\text{H}_2\text{SO}_4$ ; 10 Gm. Contain 0.689 Gm. $\text{H}_2\text{O}$	3 Dried in Air at 80° for 3 Hours; 10 Gm. Contain 1.38 Gm. $\text{H}_2\text{O}$	4 Not dried; 10 Gm. Contain 3.14 Gm. $\text{H}_2\text{O}$
5	....	....	27.0	....
10	18.2	23.9	22.7	24.5
20	15.0	....	22.5	20.1
40	13.4	18.0	22.2	20.0
60	13.2	14.7	20.8	14.0

ferrocyanide so that the action is not that of a sieve. Since the membrane is impermeable to sugar because of strong negative adsorption one might attribute the impermeability of ferrocyanide to a similar cause. This is unsatisfactory, however, since it is known that ferrocyanide ion is adsorbed sufficiently strongly by copper ferrocyanide to peptize the gel as a stable negative sol. Indeed copper ferrocyanide gel always contains alkali ferrocyanide which is retained so tenaciously that the adsorption from moderately concentrated solutions may be regarded as almost irreversible. It was suggested recently<sup>23</sup> that strong negative adsorption by the adsorption complex prevents the

<sup>19</sup> Z. physik. Chem., **10**, 255 (1892).

<sup>20</sup> Z. physik. Chem., **10**, 699 (1892).

<sup>21</sup> Donnan and Allmand: J. Chem. Soc., **105**, 1941 (1914); Donnan and Garner: *Ibid.*, **115**, 1313 (1919).

<sup>22</sup> J. Phys. Chem., **29**, 966 (1925).

<sup>23</sup> Weiser: "The Colloidal Salts," 283 (1928).

passage of both sugar and ferrocyanide through the membrane. This problem is dealt with in the following experiments.

## II. EXPERIMENTS

### DIFFUSION EXPERIMENTS

To check up the question of the alleged impermeability of copper ferrocyanide membrane to ferrocyanide ion the following experiments were carried out: Parchment thimbles 1.5 cm. in diameter and 10 cm. in length were impregnated with a copper ferrocyanide membrane by placing a  $N/5$   $K_4Fe(CN)_6$  solution on the inside of the thimble, and  $N, 5$   $CuSO_4$  on the outside. After standing for three or four days, the operation was repeated with the copper salt on the inside. The thimbles were then placed in dilute copper sulfate for a day to insure the removal of all potassium ferrocyanide, after which they were kept in contact with distilled water changed repeatedly for one week, before using. Ten-cubic-centimeter portions of solutions of potassium ferrocyanide of varying strength were placed on the inside of the membranes which were suspended in large test tubes and surrounded by sugar solutions found by trial to be isotonic with the salt solutions. Tests for ferrocyanide in the sugar solutions were made at intervals by the Prussian blue test. If the membrane was perfect at the start, it was found to be impermeable indefinitely to  $N/5$ ,  $N/3$ , and  $N/2.5$  solutions of  $K_4Fe(CN)_6$ . Most membranes failed within a few days with solutions as strong as  $N$  and  $2N$  but one membrane retained a  $N$  solution 18 days and was still good when the experiment was stopped. The greater tendency for the membrane to allow relatively high concentrations of ferrocyanide to pass is probably due to partial coagulation of the colloidal film by the salt thereby opening up cracks at weak points in an imperfectly formed membrane.

The impermeability of the membrane to ferrocyanide ion is further shown by the following ultrafiltration experiment: A good grade of parchment paper was stretched tightly over a bell-jar and impregnated with copper ferrocyanide by a suitable modification of the procedure employed for impregnating the thimbles. A 7-cm. disc of the membrane was placed in an ultrafilter, into which was poured 100 cc. of  $N/10$   $K_4Fe(CN)_6$  solution and a pressure of 150 lb. per sq. in. was applied. Filtration was very slow but 30 cc. of ferrocyanide-free filtrate was obtained before a leak developed in the filter.

## ADSORPTION EXPERIMENTS

*Adsorption of  $K_4Fe(CN)_6$  by Dried  $Cu_2Fe(CN)_6$ .*—To determine whether dried copper ferrocyanide formed in the presence of excess  $K_4Fe(CN)_6$  adsorbs ferrocyanide positively or negatively, the following experiment was carried out: A copper ferrocyanide gel was precipitated by adding a slight excess of  $K_4Fe(CN)_6$  solution to copper chloride solution and the gel washed by decantation by the aid of the centrifuge. Unfortunately, it was impossible to remove all the ferrocyanide from the supernatant solution by washing with pure water since the gel is readily peptized as a negative sol. Accordingly, the washing was carried out with 0.05 N KCl solution. The washed gel was dried on the steam bath, ground to a fine powder and a 2.5-gm. sample thoroughly mixed with 25 cc. of N/50  $K_4Fe(CN)_6$  solution. After standing several hours, a 10-cc. sample of the clear supernatant solution was titrated with potassium permanganate: 2.6 cc. of solution were required as compared with 6.75 cc. for 10 cc. of the original solution. This definite evidence of positive adsorption of ferrocyanide ion by the dry copper ferrocyanide indicates that the adsorption of ferrocyanide ion is reversible. Washing the gel formed in the presence of excess ferrocyanide removed a part of the adsorbed ion which was taken up again when the dry salt was placed in the  $K_4Fe(CN)_6$  solution. It might be argued that chloride in the wash water displaced the adsorbed ferrocyanide and that there would be no reversal of adsorption by washing with pure water. This seems altogether unlikely, however, since the adsorption of chloride is usually very much less than that of tetravalent ferrocyanide. Moreover, reversal of adsorption is strongly indicated by the peptization which follows washing of the gel with pure water. Further light is thrown on the situation by the adsorption isotherms of a number of salts with copper ferrocyanide gel as adsorbent.

*Adsorption of  $K_4Fe(CN)_6$  by  $Cu_2Fe(CN)_6$  Gel.*—Solutions of  $K_4Fe(CN)_6$  and of  $CuCl_2$  were prepared such that 50 cc. of the former was exactly equivalent to 100 cc. of the latter and on mixing the respective amounts, theoretically 0.5 gm.  $Cu_2Fe(CN)_6$  was formed. The adsorption isotherm was obtained by taking 100-cc. portions of  $CuCl_2$  solution, adding increasing amounts of  $K_4Fe(CN)_6$  solution above 50 cc., and determining the equilibrium concentration of ferrocyanide. A difficulty with the procedure is that the copper ferrocyanide gel is not precipitated in the presence of a small excess of  $K_4Fe(CN)_6$  but remains suspended as a negative sol. At the outset the concentration of the intermicellar liquid was determined by ultrafiltration of the sol through a cellophane membrane and analysis of the ultrafiltrate. It was later

found that almost identical results were obtained by increasing slightly the potassium chloride concentration of the solution, thereby preventing the peptization of the gel so that the supernatant solution could be analyzed directly for ferrocyanide. Since this procedure required much less time than that involving ultrafiltration, it was the one adopted.

The mixing of the solutions was done in a 250-cc. wide-mouth bottle. In the bottle were placed the ferrocyanide solution, 100 cc. of 2.5 N KCl, and enough water to make exactly 150 cc. One hundred cubic centimeters of the  $\text{CuCl}_2$  solution were transferred to a 200-cc. flask with a short neck 3 cm. in diameter inserted through a rubber stopper which fitted the bottle. In order to retain the solution when the flask was inverted, the neck of the latter was fitted with a thin slice of rubber cut from a stopper. To mix the solutions the neck of the flask was inserted firmly in the bottle which was given a jar, thereby dislodging the thin stopper from the neck of the flask and allowing very rapid and thorough mixing of the solutions. After standing for 24 hours and centrifuging, samples of the supernatant solutions were withdrawn and analyzed for ferrocyanide by titration with standard potassium permanganate according to the method of Müller and Diefenthaler.<sup>24</sup> Since quite dilute solutions were used in some cases, special precautions were taken to get a definite endpoint.<sup>25</sup>

The results of the observations are given in Table 2 and shown graphically in Fig. 1. The adsorption, in mols  $\text{K}_4\text{Fe}(\text{CN})_6$  per mol  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , plotted against the equilibrium concentration of  $\text{K}_4\text{Fe}(\text{CN})_6$ , in millimols per liter, is shown in the upper curve while the logarithm of the adsorption against the logarithm of the equilibrium concentration is shown in the lower curve.

These observations show the marked adsorption of copper ferrocyanide gel for potassium ferrocyanide. Thus it will be seen that approximately 0.45 mol  $\text{K}_4\text{Fe}(\text{CN})_6$  per mol of  $\text{Cu}_2\text{Fe}(\text{CN})_6$  is taken up before the equilibrium concentration of  $\text{K}_4\text{Fe}(\text{CN})_6$  in contact with the gel is appreciable. It has been well known for a long time that  $\text{Cu}_2\text{Fe}(\text{CN})_6$  cannot be prepared pure by the interaction of  $\text{CuCl}_2$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ . Thus Duclaux<sup>26</sup> claims that the formula for the precipitate must be represented by the general formula  $\text{Cu}_m\text{K}_n\text{Fe}(\text{CN})_6$  when  $m + n/2 = 2$ . Duclaux believes the potassium ferrocyanide to be combined with the copper salt forming a series of definite double salts. It seems more likely, however, that the gel is copper ferrocyanide with potassium ferrocyanide adsorbed in varying amounts, depending on the

<sup>24</sup> Z. anorg. Chem., 67, 418 (1910).

<sup>25</sup> Weiser and Sherrick: J. Phys. Chem., 23, 205 (1919).

<sup>26</sup> J. chim. phys., 5, 29 (1907).

TABLE 2.—ADSORPTION OF  $K_4Fe(CN)_6$  BY  $Cu_2Fe(CN)_6$ 

Solutions Mixed Total Volume, 250 Cc.)		Equilibrium Concentration of $K_4Fe(CN)_6$ Millimols per Liter	$K_4Fe(CN)_6$ Adsorbed	
$CuCl_2$	$K_4Fe(CN)_6$		Grams per Gram	Mols per Mol
100	50	0.0	0.0000	0.0000
100	60	0.0	0.2172	0.2000
100	70	0.0	0.4344	0.4000
100	75	0.0692	0.5292	0.4872
100	80	0.2308	0.6080	0.5598
100	90	0.9486	0.6932	0.6382
100	100	1.9237	0.7308	0.6728
100	140	6.2705	0.7994	0.7360
100	140	22.0763	0.9286	0.8550

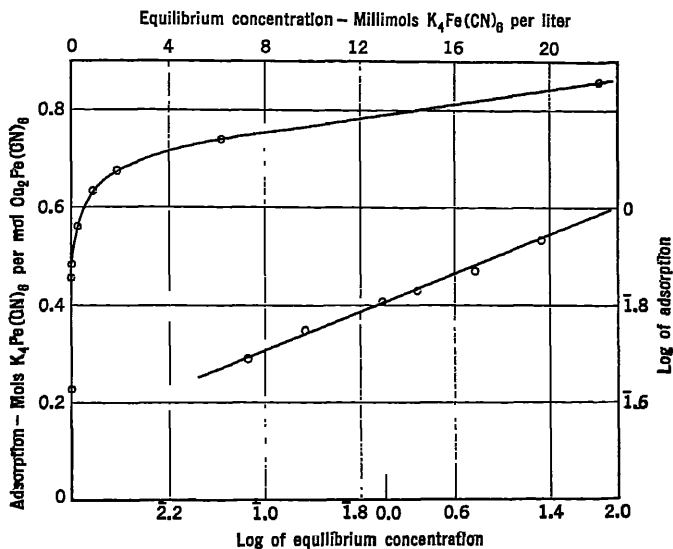


FIG. 1.—Adsorption of potassium ferrocyanide by copper ferrocyanide.

ve concentrations of the salts and the conditions of precipitation. does not preclude the formation of definite double salts under n conditions; but the composition of the precipitated gel can be d continuously over such a wide range that one is not justified in ding that a double salt is formed simply from the analysis of an phous mass.

From the form of the adsorption isotherm shown in Fig. 1, it might be argued that a definite double salt was formed of the composition  $5\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 2\text{K}_4\text{Fe}(\text{CN})_6$  or  $\text{Cu}_{10}\text{K}_8[\text{Fe}(\text{CN})_6]_7$  and that the upper portion of the curve represents the adsorption of  $\text{K}_4\text{Fe}(\text{CN})_6$  by this double salt. While this might be true, there is no evidence to date to support it. Numerous crystalline alkali-and alkaline earth-cupric ferrocyanides have been described by Bolley,<sup>27</sup> Wonfor,<sup>28</sup> and Wyruboff,<sup>29</sup> but Messner<sup>30</sup> showed that the only ones that exist have the simple formula  $\text{X}'_2\text{CuFe}(\text{CN})_6$  where  $\text{X} = \text{K}, \text{Na}$  and  $\text{NH}_4$ , or  $\text{X}''\text{CuFe}(\text{CN})_6$  where  $\text{X}'' = \text{Mg}, \text{Ca}, \text{Sr}$  and  $\text{Ba}$ . A further indication that the gel obtained as described above does not contain a double salt is furnished by the curve Fig. 1, using logarithmic coordinates. The points are found to lie more nearly on a straight line if the adsorption values are taken as given instead of subtracting from each a constant value, say 0.4. This indicates that the adsorption curve actually passes through the origin and that the equilibrium concentration approaches but does not reach zero when the adsorption is between 0.0 and 0.45 mol  $\text{K}_4\text{Fe}(\text{CN})_6$  per mol of copper salt. In this region a more delicate analytical method would be required to show the variation from zero concentration of  $\text{K}_4\text{Fe}(\text{CN})_6$  in the supernatant solution.

*Adsorption of  $\text{Na}_4\text{Fe}(\text{CN})_6$  by  $\text{Cu}_2\text{Fe}(\text{CN})_6$  Gel.*—The adsorption of sodium ferrocyanide was determined by the same procedure described in the previous section. The results are given in Table 3 and shown graphically in Fig. 2. The form of the adsorption isotherm is very similar to that of the corresponding potassium salt but the adsorption is appreciably less.

*Adsorption of  $\text{H}_4\text{Fe}(\text{CN})_6$  by  $\text{Cu}_2\text{Fe}(\text{CN})_6$  Gel.*—It is claimed that pure copper ferrocyanide can be prepared by adding an excess of  $\text{CuCl}_2$  to  $\text{H}_4\text{Fe}(\text{CN})_6$  solution.<sup>31</sup> This would indicate that  $\text{H}_4\text{Fe}(\text{CN})_6$  is adsorbed by the gel much less strongly than the sodium or potassium salts. Such was found to be the case.

Hydroferrocyanic acid is somewhat difficult to work with since its solutions oxidize rapidly in the air and even when dissolved in oxygen-free water, it undergoes an internal oxidation-reduction reaction with the formation of Prussian blue and the liberation of hydrocyanic acid. The pure stable crystals were obtained in the following way: Approximately 40 gm. of potassium ferrocyanide were placed in a glass-stoppered bottle

<sup>27</sup> Liebig's Ann., 106, 228 (1858).

<sup>28</sup> Jahresber., 233 (1862).

<sup>29</sup> Ann. chim. phys., (5) 8, 444 (1876).

<sup>30</sup> Z. anorg. Chem., 8, 368 (1895).

<sup>31</sup> Williams: "The Chemistry of Cyanogen Compounds," (1915).

TABLE 3—ADSORPTION OF  $\text{Na}_4\text{Fe}(\text{CN})_6$  BY  $\text{Cu}_2\text{Fe}(\text{CN})_6$ 

Solutions Mixed (Total Volume, 250 Cc.)		Equilibrium Concentration of $\text{Na}_4\text{Fe}(\text{CN})_6$ , Millimols per Liter	$\text{Na}_4\text{Fe}(\text{CN})_6$ Adsorbed	
$\text{CuCl}_2$	$\text{Na}_4\text{Fe}(\text{CN})_6$ , 9.74 Gm. per Liter		Grams per Gram	Mols per Mol
100	60	0.0617	0.2632	0.2937
100	70	0.6336	0.3710	0.4139
100	75	1.0993	0.3977	0.4437
100	80	1.6260	0.4150	0.4630
100	90	2.7177	0.4439	0.4953
100	100	3.9313	0.4543	0.5069
100	140	8.7804	0.4969	0.5544

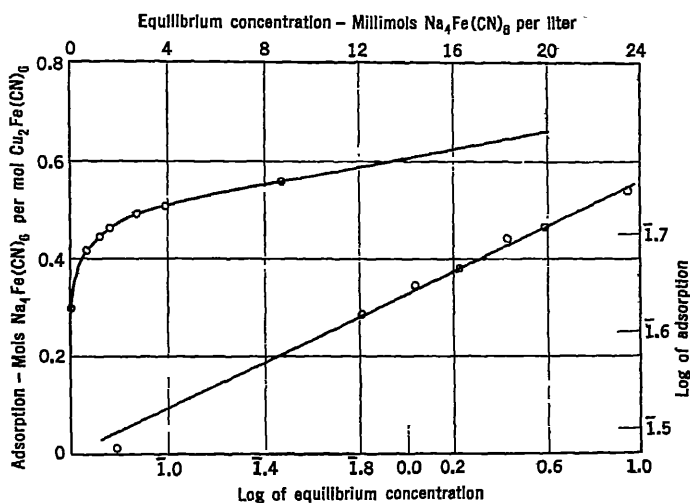


FIG. 2.—Adsorption of sodium ferrocyanide by copper ferrocyanide.

and dissolved in 200 cc. of freshly boiled and cooled distilled water. To this was added slightly more than the equivalent amount of concentrated hydrochloric acid. If any KCl precipitated, it was dissolved by the addition of a small amount of water. Fifty cubic centimeters of cold ether were then added to the bottle which was stoppered and shaken gently with a whirling motion in order to bring the ether slowly in contact with the solution. By this procedure the hydroferrocyanic acid was precipitated as a coarse crystalline mass which was transferred rapidly to a Buchner funnel and washed with dilute hydrochloric acid

containing a large amount of ether and, finally, with pure ether. When the crystals appeared dry they were placed on an unglazed plate in a vacuum desiccator over sulfuric acid. After evacuating with a water pump until most of the ether was removed, as high a vacuum as possible was maintained with an oil pump. When the product was thoroughly dry it was transferred to a glass-stoppered bottle which was kept in a vacuum desiccator. The acid formed in this way was almost white and was quite stable in the absence of moisture.

The adsorption of the acid by  $\text{Cu}_2\text{Fe}(\text{CN})_6$  gel was determined in the same way as the adsorption of its salts except that the precipitations and analyses were made as soon as possible after making up the  $\text{H}_4\text{Fe}(\text{CN})_6$  solution before marked decomposition of the acid had taken place. Ten cubic centimeters of  $\text{N HCl}$  in 250 cc. were sufficient to prevent peptization of the gel. The results of the observations are given in Table 4 and shown graphically in Fig. 3.

It will be noted that hydroferrocyanic acid is adsorbed much less than its salts by the copper ferrocyanide gel. The adsorption curve touches the  $x$ -axis a relatively small distance above the origin. This suggests that a copper ferrocyanide membrane made by the action of  $\text{CuCl}_2$  and  $\text{H}_4\text{Fe}(\text{CN})_6$  may be slightly permeable to the acid. The membranes were prepared in parchment as previously described, replacing the hydroferrocyanic solution whenever it had taken on a deep blue color. After thorough washing,  $\text{N}/10$  hydroferrocyanic acid solution was placed on the inside of the stoppered thimble and sugar solution on the outside. After several days, during which the acid solution was changed repeatedly, a faint test for ferrocyanide ion was obtained in the sugar solution. It was impossible to carry out the experiments in a satisfactory manner because of the instability of the acid which decomposed in the pores of the membrane clogging them with Prussian blue.

An attempt was made to show the extent of the permeability of the membrane to the acid in another way: Solutions of  $\text{CuCl}_2$ ,  $\text{N}/10$  and  $\text{N}/4$  were made up in 10 per cent gelatin solution, at  $40^\circ$ . After filtering through sand to remove air bubbles, the solutions were placed in test tubes and allowed to set. Equivalent solutions of  $\text{K}_4\text{Fe}(\text{CN})_6$  and of  $\text{H}_4\text{Fe}(\text{CN})_6$  were poured on the sample of gel and the behavior observed. In all cases a film of copper ferrocyanide formed at once and grew in thickness as the copper diffused up and met the ferrocyanide. With the hydroferrocyanic acid a clear space appeared below the membrane in a short time, and finally rhythmic bands resulted. The appearance of these bands is shown in the photograph reproduced in Fig. 4. For comparison, the tube containing  $\text{K}_4\text{Fe}(\text{CN})_6$  was photographed at the



TABLE 4.—ADSORPTION OF  $\text{H}_4\text{Fe}(\text{CN})_6$  BY  $\text{Cu}_2\text{Fe}(\text{CN})_6$ 

Solutions Mixed (Total Volume, 250 Cc.)		Equilibrium Concentration of $\text{H}_4\text{Fe}(\text{CN})_6$ , Millimols per Liter	$\text{H}_4\text{Fe}(\text{CN})_6$ Adsorbed	
$\text{CuCl}_2$	$\text{H}_4\text{Fe}(\text{CN})_6$		Grams per Gram	Mols per Mol
100	50	0.0	0.0	0.0
100	53 3	0.0575	0.0360	0.0564
100	55	0.1270	0.0499	0.0784
100	60	0.5307	0.0700	0.1098
100	70	1.477	0.0950	0.1492
100	90	3.540	0.1272	0.1997
100	100	4.693	0.1299	0.2038
100	140	9.233	0.1493	0.2346
100	140	25.460	0.1797	0.2820

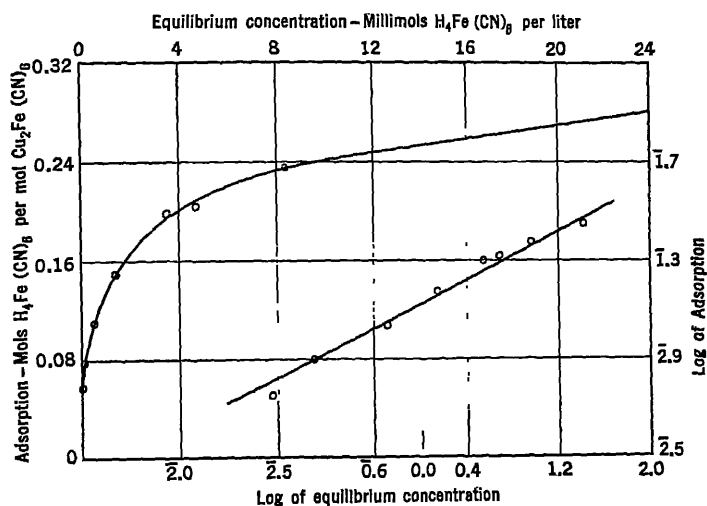


FIG. 3.—Adsorption of hydroferrocyanic acid by copper ferrocyanide.

it of that containing  $\text{H}_4\text{Fe}(\text{CN})_6$ . It will be seen that there is no  
of rhythmic banding with  $\text{K}_4\text{Fe}(\text{CN})_6$ . The bands were a grayish-  
te by reflected light but brown by transmitted light, indicating that  
y were deposits of finely divided copper ferrocyanide formed by  
usion of the acid through the membrane and reaction with copper  
ride. Later tests showed, however, that the bands were not copper  
ocyanide but were copper cyanide resulting from the diffusion of

hydrocyanic acid formed by the spontaneous decomposition of the  $\text{H}_4\text{Fe}(\text{CN})_6$ .

In the light of these observations all that one can say is that  $\text{H}_4\text{Fe}(\text{CN})_6$  may diffuse very slowly through a copper ferrocyanide membrane, but because of the spontaneous decomposition with the formation of Prussian blue and hydrocyanic acid, the extent of the diffusion cannot be determined.

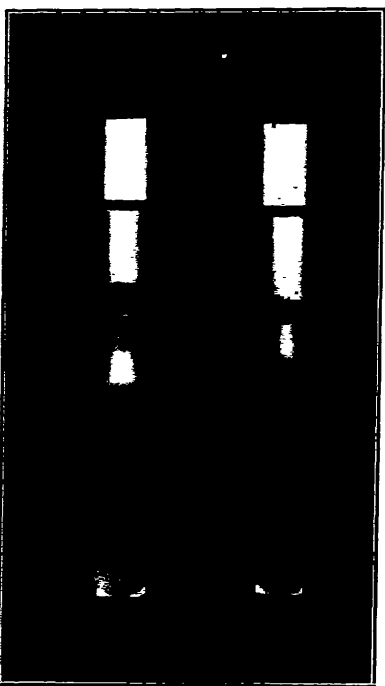


FIG. 4.—Rhythmic bands formed by the action of hydroferrocyanic acid on copper chloride in gelatin.

*Adsorption of  $\text{CuCl}_2$  by  $\text{Cu}_2\text{Fe}(\text{CN})_6$  Gel.*—Walden<sup>32</sup> reported that copper ferrocyanide is impermeable to copper ion as well as to ferrocyanide ion. These observations were responsible for the quite generally accepted view that a gelatinous membrane is impermeable to its own ions. Tests with membranes supported in parchment thimbles disclosed that copper ferrocyanide is readily permeable to copper ion. Walden formed his membranes in gelatin and had the membrane-forming reagents on either side during his tests of permeability. It is probable that he failed to observe the passage of copper ion through the membrane because of his failure to remove all ferrocyanide which would react with the copper ion as fast as it came through.

Since copper ion passes through the membrane, it was of interest to compare the adsorption isotherm for a copper salt with that of a ferrocyanide. The procedure was the same as that previously used except that a constant amount of ferrocyanide (equivalent to 0.5 gm.  $\text{Cu}_2\text{Fe}(\text{CN})_6$ ) was employed and the amount of  $\text{CuCl}_2$  was varied. An attempt was first made to use  $\text{K}_4\text{Fe}(\text{CN})_6$ , but the adsorption of the salt was so strong that copper ion was always left over when  $\text{CuCl}_2$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  were mixed in equivalent amounts.  $\text{H}_4\text{Fe}(\text{CN})_6$  solution was therefore employed. Copper ion was determined electrolytically after the copper chloride solutions were taken to dryness and converted

<sup>32</sup> Z. physik. Chem., 10, 699 (1892).

to sulfate with sulfuric acid. The results are given in Table 5 and plotted in Fig. 5. It is clear that the adsorption is very small compared to that of hydroferrocyanic acid or its salts. As we shall see, this is significant for the theory of the semipermeable membrane.

TABLE 5—ADSORPTION OF  $\text{CuCl}_2$  BY  $\text{Cu}_2\text{Fe}(\text{CN})_6$ 

Solutions Mixed (Total volume, 250 Cc.)		Cu Remaining in 200 Cc., Gram	Equilibrium Concentration of $\text{CuCl}_2$ , Millimols per Liter	CuCl <sub>2</sub> Adsorbed	
CuCl <sub>2</sub>	$\text{H}_4\text{Fe}(\text{CN})_6$			Grams per Gram	Mols per Mol
55	50	0.0150	1.173	0.00	0.00
60	50	0.0291	2.290	0.0046	0.0044
70	50	0.0583	4.586	0.0090	0.0088
85	50	0.1029	8.092	0.0110	0.0108
100	50	0.1475	11.602	0.0130	0.0128
150	50	0.2970	22.543	0.0156	0.0154

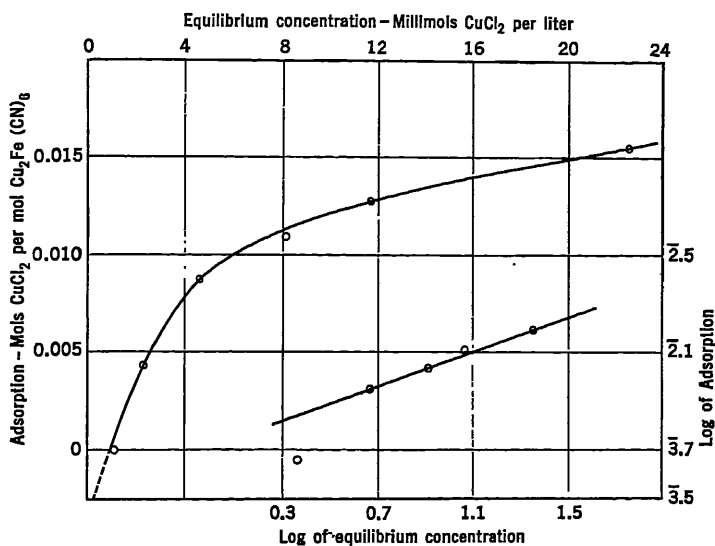


FIG. 5.—Adsorption of copper chloride by copper ferrocyanide.

Professor Hulett told me of his attempt to make a standard cell with approximately zero temperature coefficient according to the scheme:  $\text{Zn}|\text{ZnSO}_4||\text{CuSO}_4|\text{Cu}$ . An essential feature of the proposed cell was a membrane between the solutions consisting of a mixture of the ferro-

cyanides of zinc and copper which was expected to prevent the interdiffusion of the ions. The cell proved to be unsatisfactory since, as we now know, the ferrocyanides of zinc and copper are permeable to the respective cations.

*Adsorption of  $K_2SO_4$  by  $Cu_2Fe(CN)_6$  Gel.*—Tammann<sup>33</sup> and Walden<sup>34</sup> claim that copper ferrocyanide is impermeable to alkali, alkaline earth, and heavy metal sulfates, but is permeable to sulfuric acid. Tests carried out as previously described showed, however, that the membrane is permeable to the sulfates of potassium, sodium, copper, and magnesium; and it is probable that any sulfate will diffuse through.

The adsorption of sulfate was determined for a gel thrown down by the action of  $CuCl_2$  and  $H_4Fe(CN)_6$  in the presence of potassium sulfate. The analyses were made gravimetrically as  $BaSO_4$ . The results are given in Table 6 and plotted in Fig. 6. It will be seen that  $K_2SO_4$  is adsorbed slightly more than  $CuCl_2$ , but very much less than hydroferrocyanic acid or its salts. Walden's observation that sulfuric acid would diffuse through a ferrocyanide membrane but that its alkali salts would not, is but one example of a large group which he investigated. Thus he reports that the membrane is permeable to N/10 solutions of the following acids but not to the salts of the acids: formic, acetic, propionic, butyric, isobutyric, valerianic, cyanacetic, halogen acetic acids, glycolic, methyl- and ethyl-glycolic, phenyl glycolic, diglycolic, glyoxalic,  $\alpha$  and  $\beta$  oxypropionic, glyceric,  $\alpha$  and  $\beta$  oxybutyric, meta and para oxybenzoic, quinic, tartaric, citric, mandelic,  $\alpha$ -nitrophthalic, mellitic, tetracarboxylic, dimethyl malonic, quinolinic, sulfanilic, methylenedisulfonic, quinolinesulfonic, xylo-, benzol-, pseudocumol- and naphthalene sulfonic acids, sulfuric, chromic, dimethyl phosphoric, phosphoric, arsenotungstic, phosphotungstic, arsenomolybdic, borotungstic, acrylic, caproic, and colloidal tungstic acid.

There appears to be no good reason why the acids should diffuse through the membrane, and not the alkali salts. Bancroft and Gurchot<sup>35</sup> believe that the acids may have a coagulating action on the membrane which will render it permeable; but it is more probable that Walden's observations are open to question, owing to the limitations of his experimental method. Certainly this is the case with sulfuric acid and sulfates. Walden placed potassium ferrocyanide containing sensitive blue litmus on one side of a membrane formed in gelatine, and copper sulfate with N/10 solutions of the acids on the opposite side, and noted whether or not the blue litmus turned red within an hour. That it did

<sup>33</sup> Z. physik. Chem., 10, 255 (1892).

<sup>34</sup> Z. physik. Chem., 10, 699 (1892).

<sup>35</sup> J. Phys. Chem., 28, 1279 (1924); 30, 83 (1926).

TABLE 6.—ADSORPTION OF  $K_2SO_4$  BY  $Cu_3Fe(CN)_6$ 

$K_2SO_4$ Added, 0.05 Molar	$BaSO_4$ in 200 Cc.	Equilibrium Concentration of $K_2SO_4$ , Millimols per Liter	$K_2SO_4$ Adsorbed	
			Grams per Gram	Mols per Mol
5	0.0465	0.996	0.00046	0.0009
10	0.0918	1.965	0.0030	0.0058
20	0.01830	3.932	0.0072	0.0139
35	0.3206	6.868	0.0114	0.0224
50	0.4595	9.844	0.0138	0.0267
100	0.6924	14.835	0.0148	0.0288

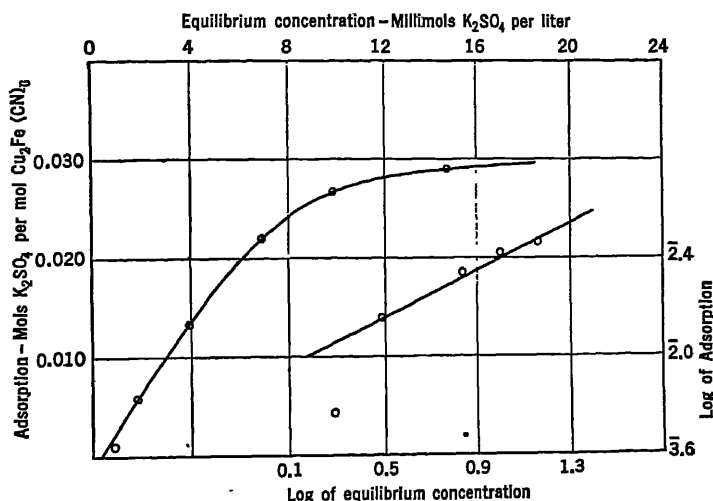


FIG. 6.—Adsorption of potassium sulfate by copper ferrocyanide.

with the acids investigated is what one might expect since the tendency to set up a Donnan equilibrium would cause the rapidly moving hydrogen ion to pass through the membrane and turn the litmus. No such test was available when the sodium salts were employed and so they were reported as not diffusing. It is obvious that Walden observed the diffusion of hydrogen ion and not of the anions. His experiments tell us only that the degree of ionization of the acids employed was such that in one hour sufficient hydrogen ion diffused through the membrane to change a part of the litmus from blue to red.

Further doubt is thrown on the accuracy of Walden's experimental method by the observation that sufficient colloidal  $MoO_3$  passed through

the membrane in an hour to give the molybdenum blue test on reduction with zinc. While it may be that the particles of colloidal  $\text{MoO}_3$  are small enough to pass a well-formed membrane if sufficient time is allowed, it is unlikely that any appreciable amount would go through in an hour unless the membrane was defective.

While Walden's data are not satisfactory, it is likely that most, if not all, of the above mentioned acids as well as their alkali salts will pass through a copper ferrocyanide membrane if sufficient time is allowed. A preliminary test showed that in ten days both phosphomolybdic acid and sodium phosphomolybdate had passed through a membrane into isotonic sugar solution, in sufficient amount to give a distinct molybdenum blue test. The membranes employed were found to be impermeable to potassium ferrocyanide both before and after the experiments with phosphomolybdate. Since alkali phosphomolybdate molecules are very large compared to alkali ferrocyanide, the impermeability of copper ferrocyanide to the latter is clearly not a question of pore size.

### III. DISCUSSION OF RESULTS

A membrane which may be regarded as continuous as distinct from porous will be permeable to the solvent and not to the solute if the former dissolves in the membrane and the latter does not. A distinctly porous membrane will be permeable to the solvent and not to the solute if it exhibits such marked negative adsorption that the pore walls are covered with a film of pure solvent and if the pores are sufficiently fine that the adsorbed film fills the pores full. An example of the first class is rubber which is highly permeable to benzene, toluene, and pyridine, which are readily soluble in it, and almost impermeable to water, which is but slightly soluble in it. An example of the second class is copper ferrocyanide which is permeable to water but not to sugar.

The copper ferrocyanide membrane is impermeable to potassium and sodium ferrocyanide and but slightly permeable, if at all, to hydroferrocyanic acid. This is not due to strong negative adsorption as in the case of sugar solution. On the contrary, the adsorption of ferrocyanides by copper ferrocyanide gel is unusually great. Thus in the case of potassium ferrocyanide the adsorption is so strong that it is practically irreversible between 0 and 0.4 mol of  $\text{K}_4\text{Fe}(\text{CN})_6$  per mol of  $\text{Cu}_2\text{Fe}(\text{CN})_6$ . Therein lies the explanation of the impermeability of the membrane to ferrocyanide. The adsorption is so strong that the fixed walls of the pores hold chains of oriented ferrocyanide molecules extending from a monomolecular film on the surface throughout the pore solution. The practically irreversibly adsorbed ferrocyanide is sufficient to saturate the pore water with the salt. The condition is represented

diagrammatically in Fig. 7 in which the dark circles represent ferrocyanide molecules. Since the solution in the pores is saturated with the adsorbed salt, no more ferrocyanide can enter from the side of the membrane in contact with the solution; and since the adsorption necessary to saturate the pore solution is practically irreversible, ferrocyanide will not pass into water or sugar solution on the opposite side. The result is that the membrane will be impermeable to solute but not to the solvent.

Turning to copper chloride and potassium sulfate, we find that these salts are likewise adsorbed by copper ferrocyanide gel but the membrane is permeable to them, nevertheless. The reason for this is indicated by Fig. 8, which shows the adsorption isotherms of the several salts all plotted on the same scale. It will be seen that copper chloride and potassium sulfate are adsorbed very much less strongly than the ferrocyanides. Moreover, the relatively weak adsorption of the former salts is practically completely reversible throughout the entire range. Since the adsorption is insufficient to saturate the solvent in the pores and since the adsorption is reversible, copper chloride and potassium sulfate will diffuse through the membrane. Between one extreme, that of potassium ferrocyanide which will not pass the membrane owing to strong adsorption which is irreversible throughout a certain range, and the other extreme, that of copper chloride which passes the membrane because of relatively weak adsorption which is completely reversible, there are an indefinite number of gradations in the degree of permeability as a result of positive adsorption. The copper ferrocyanide membrane should be more permeable to hydroferrocyanic acid than its alkali salts but the instability of solutions of the acid makes it difficult to carry out comparative tests. A quantitative study is now being made of the relationship between the permeability of a membrane for salts and the adsorption of the salts by the membrane. In this connection Hartung<sup>30</sup> reports that potassium chloride is adsorbed by copper ferrocyanide less strongly than is potassium sulfate and that the former diffuses through

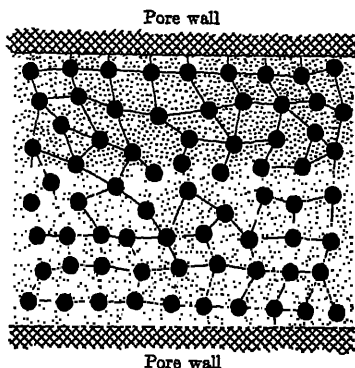


FIG. 7.—Diagrammatic representation of a portion of a pore in a copper ferrocyanide membrane in which the pore water is saturated with adsorbed potassium ferrocyanide.

<sup>30</sup> Trans. Faraday Soc., 15 (3), 160 (1920).

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membrane more rapidly than the latter. This appears to be in  
d with what one might expect.

the adsorption of the ferrocyanides by copper ferrocyanide is in the  
:  $K_4Fe(CN)_6 > Na_4Fe(CN)_6 > H_4Fe(CN)_6$ . It seems probable

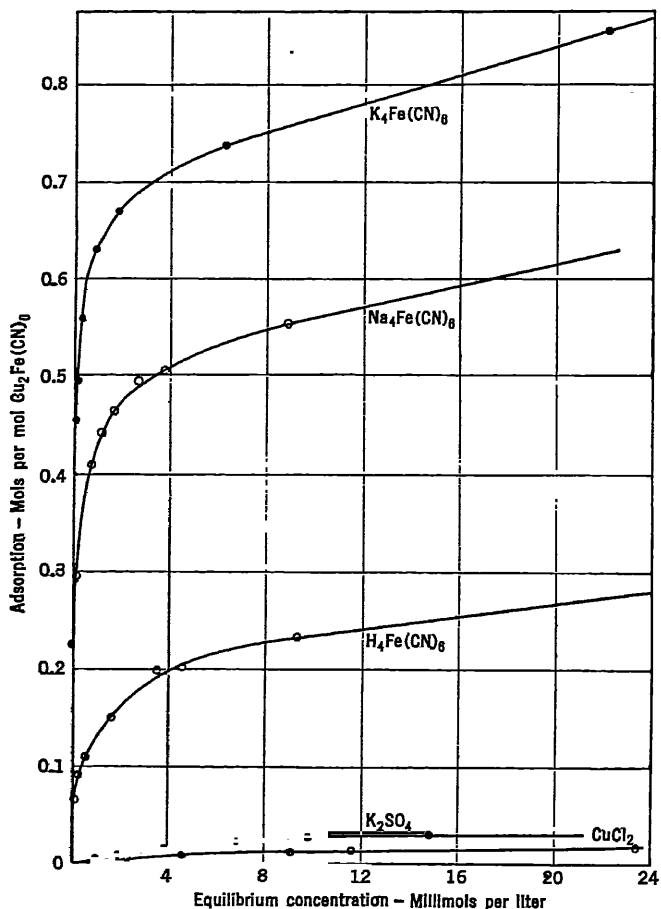


FIG. 8.—Adsorption by copper ferrocyanide.

the variation in adsorption is due to the difference in hydration of  
pective cations. If one accepts Fajans'<sup>37</sup> view that the hydra-  
an ion consists in the formation of a polarized water envelope,  
process being accompanied by a positive heat effect, one should  
the adsorption to be accompanied by a partial dehydration, the  
turwissenschaften, 37, 1 (1921).



extent of which will be determined by the heat of hydration of the ions. Since the heat of hydration and the amount of hydration decreases in the alkali series from lithium to caesium, it would follow that the adsorption would decrease in the reverse order. Actually we find the adsorption of potassium ferrocyanide to be much greater than that of the more highly hydrated sodium salt. If this is the important factor in determining the order of adsorption of the ferrocyanides, it would follow that hydrogen ion is more highly hydrated than the alkalies. This is in line with the views of Fajans,<sup>37</sup> Bjerrum,<sup>38</sup> and Schreiner.<sup>39</sup>

In conclusion, a distinctly porous membrane will be semipermeable under two conditions: (1) if the membrane exhibits such marked negative adsorption for the solute that the pore walls are covered with a film of pure solvent which completely fills the pores; and (2) if the positive adsorption of the solute is sufficiently great to saturate the solution in the pores within the range that the adsorption is practically irreversible.

#### SUMMARY

The results of this investigation may be summarized briefly as follows:

1. A porous membrane will be permeable to the solvent and not to the solute if it exhibits such marked negative adsorption that the pore walls are covered with a film of pure solvent and if the pores are sufficiently fine that the adsorbed film fills the pores full. Thus, copper ferrocyanide membrane is permeable to water but not to sugar because of strong negative adsorption.

2. A copper ferrocyanide membrane is impermeable to alkali ferrocyanides and but slightly permeable, if at all, to hydroferrocyanic acid. This is not due to negative adsorption by the membrane and is not the result of a sieve action.

3. Copper ferrocyanide gel adsorbs ferrocyanides very strongly. The adsorption of potassium ferrocyanide is so great that it is practically irreversible between 0 and 0.4 to 0.45 mol of adsorbed  $K_4Fe(CN)_6$  per mol of  $Cu_2Fe(CN)_6$ .

4. The explanation of the impermeability of copper ferrocyanide to ferrocyanides is as follows: The adsorption of ferrocyanide is so strong that the fixed walls of the pores hold chains of oriented ferrocyanide molecules extending from a monomolecular film on the surface throughout the pore solution. The practically irreversibly adsorbed ferrocyanide

<sup>38</sup> Z. anorg. Chem., **109**, 275 (1920).

<sup>39</sup> Z. anorg. Chem., **135**, 333 (1924).

is sufficient to saturate the pore water with the salt. Since the solution in the pores is saturated with the adsorbed salt, no more ferrocyanide can enter from the side of the membrane in contact with the solution and since the adsorption necessary to saturate the pore solution is practically irreversible, ferrocyanide will not pass into water or sugar solution on the opposite side. The result is that the membrane will be impermeable to the solute but not to the solvent.

5. The order of adsorption of ferrocyanides by copper ferrocyanide is:  $K_4Fe(CN)_6 > Na_4Fe(CN)_6 > H_4Fe(CN)_6$ . This is the order of increasing hydration of the cations.

6. Copper ferrocyanide is permeable to potassium sulfate and copper chloride. These salts are adsorbed relatively weakly by copper ferrocyanide gel and the adsorption is reversible.

7. A distinctly porous membrane will be semipermeable under two conditions: (1) if the membrane exhibits such marked negative adsorption for the solute that the pore walls are covered with a film of pure solvent which completely fills the pores; and (2) if the positive adsorption of the solute is sufficiently great to saturate the solution in the pores within the range that the absorption is practically irreversible. Between the two extreme conditions which produce semipermeability, there are an indefinite number of gradations in degree of permeability of a membrane for a dissolved solute.

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